THE

QUARTERLY JOURNAL

OF

THE CHEMICAL SOCIETY

OF

LONDON.

ROYAL DUBLIN SOCIETY

Committee of Publication.

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VOL. VII.

LONDON:
HIPPOLYTE BAILLIERE, 219, REGENT STREET,
AND 290, BROADWAY, NEW YORK, U.S.
PARIS: J. B. BAILLIERE, RUE HAUTEFEUILLE.
MADRID: BAILLY BAILLIERE, CALLE DEL PRINCIPE.
1855.

London:
Wilson and Ogilvy,
Skinner Street.

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The COUNCIL of the CHEMICAL SOCIETY have made an arrangement with the ROYAL SOCIETY, by which the Fellows of the Chemical Society will receive the "Proceedings of the Royal Society," from the commencement of the New Series in the present year, *free of charge.*

The Council call the attention of Fellows to the facility afforded by these "Proceedings" for the early publication of scientific intelligence. Communications intended for them, from Fellows of the Chemical Society, may be made through the Secretary, B. C. BRODIE, Esq., F.R.S. Publication of and notice in the "Proceedings" will not preclude the subsequent publication of a more extended paper either in the "Journal" of this Society, or in the Royal Society's "Transactions."

Signed, for the Council,

B. C. BRODIE,
Hon. Sec.

CHEMICAL SOCIETY, 5 CAVENDISH SQUARE,
JAN. 1, 1855.

THE

QUARTERLY JOURNAL

OF THE

CHEMICAL SOCIETY.

I.—*On the Constitution of Acids and Salts.*

By William Odling, M.B., F.C.S.,

LECTURER ON NATURAL PHILOSOPHY AND DEMONSTRATOR OF CHEMISTRY AT GUY'S HOSPITAL.

The object of this communication is to show, how all salts, whether acid, neutral, or basic, whether containing metallic protoxides, binoxides, sesquioxides, or teroxides, whether monobasic, bibasic, or tribasic, may be respectively reduced to the type of one or more atoms of water, representing water as $\left.\begin{matrix}H\\H\end{matrix}\right\}O$.

It has, I believe, been shown by the researches of Messrs. Williamson and Gerhardt, that the ethers, alcohols, and organic acids not only may, but must be reduced to this type. The notions here brought forward were originally suggested by their papers, and may be considered in great measure as elaborations of views introduced by them from time to time to the notice of this Society. I believe, however, that the formulæ I have ventured to accord to the phosphates, are quite original.

The representation of monobasic salts as homologues of water $\left(\left.\begin{matrix}NO_2\\K\end{matrix}\right\}O\right.$ nitrate of potash,$\left.\right)$ is now I believe, not unusual. Dr. Williamson has also given illustrations of the mode of representing bibasic salts in a similar manner; but in the illustrative salts brought forward by him, the bibasic characters of the salts depended entirely upon the bibasic nature of their acid

constituents, the representation of bibasic salts—bibasic from the nature of their bases—being, I believe, unattended to. With regard to Gerhardt's experiments upon the anhydrous acids, an objection has been raised to them, to the effect, that the new compounds procured by his new process need not necessarily stand to their respective hydrated acids in the same relation that the well-known anhydrous acids stand to their hydrates, or, in other words, that he, by his new process, has not produced any previously recognised anhydrous acid, but simply certain compounds which, after all, may perhaps be only isomeric with the true anhydrous acids. With the view of refuting any such objection, I sought for a method of making some well-known anhydrous acid, on a plan similar to that which he adopted for preparing his new anhydrides. For this purpose I availed myself of a new substance (a product of some experiments made by Mr. Abel and myself) viz., the bromosulphuric acid, a white, solid, crystalline volatile body, analogous to Regnault's chlorosulphuric acid.

This substance was sealed in a tube with excess of sulphate of silver, and heated in an oil-bath. Bromide of silver and anhydrous sulphuric acid resulted, in the same manner as, by heating chloride of benzoyl and benzoate of soda, we obtain chloride of sodium and anhydrous benzoic acid.

$$\mathrm{Bz\,Cl} + \left.\begin{matrix}\mathrm{Bz}\\ \mathrm{K}\end{matrix}\right\}\mathrm{O} = \begin{matrix}\mathrm{K}\\ \mathrm{Cl}\end{matrix} + \left.\begin{matrix}\mathrm{Bz}\\ \mathrm{Bz}\end{matrix}\right\}\mathrm{O}$$

$$\mathrm{SO_2\,Br_2} + \left.\begin{matrix}\mathrm{SO_2}\\ \mathrm{2\,Ag}\end{matrix}\right\}\mathrm{O_2} = 2\begin{matrix}\mathrm{Ag}\\ \mathrm{Br}\end{matrix} + \left.\begin{matrix}\mathrm{SO_2}\\ \mathrm{SO_2}\end{matrix}\right\}\mathrm{O_2}$$

the only difference between the two equations being, that the one represents the formation of a monobasic, and the other that of a bibasic anhydride.

For the building up of the formulæ I am about to submit to you, it is necessary—to accord to different substances different representative values, and occasionally to the same substance under different conditions, likewise different representative values—to avail myself of an illustration made use of by Dr. Williamson on a previous occasion in the case of tin. The atom of tin has usually a replaceable, or representative, or substitution value, equal to that of hydrogen, as seen in the formulæ H Cl and Sn Cl; but, under certain circumstances, its equivalent becomes, as it were, doubled, and in substitutions the atom of tin has a representative value equal to that of 2 atoms of hydrogen, as seen in the formulæ H H Cl_2 and Sn Cl_2.

In the same manner iron has two replaceable values, equal respectively to 1 and $1\frac{1}{2}$ atoms of hydrogen; bismuth a representative value equal to 3 atoms of hydrogen; mercury and copper two representative values, and so on. Now for the clear elucidation of the succeeding formulæ, I adopt in them, a simple plan of marking these different substitution values, viz., by one or more dashes to the right or left of the symbol, something after the fashion frequently made use of in algebraical formulæ: thus,

H′, an atom of hydrogen.

Sn′, an atom of tin, as existing in stannous salts, having a substitution value equal to that of hydrogen.

Sn″, the same atom of tin, having the same atomic weight, but existing in stannic salts, and having a substitution value equal to that of 2 atoms of hydrogen.

Bi‴, an atom of bismuth, as existing in bismuth salts, having a value represented by 3 atoms of hydrogen.

Fe′, an atom of iron, as existing in ferrous salts, having a replaceable value equal to that of hydrogen.

Fe Fe‴ or Fe'''_2, 2 atoms of iron, as existing in ferric salts, having together a substitution value equal to that of 3 atoms of hydrogen.

Hg′, an atom of mercury, as existing in mercuric salts, having a substitution value equal to that of hydrogen.

„Hg, an atom of mercury, as existing in mercurous salts, having only half the replaceable value of an atom of hydrogen.

From this it is evident that in making equivalent substitutions for 1, 2, or 3 atoms of hydrogen respectively, the number of atoms introduced may vary very considerably, provided the total exponential value remains the same: thus, 3 atoms of hydrogen, H′ H′ H′, may be alike perfectly represented by

K′ K′ K′
$1\frac{1}{2}$ Sn″
Sn″ + K′
Fe Fe‴
Bi‴
6 „Hg

in each of which cases, the same exponential value is maintained, notwithstanding the difference in the numbers of the atoms.

I proceed to offer some general illustrations of compounds formed on the types of 1, 2, and 3 atoms of water respectively.

One atom of water being taken as the type

$$\left.\begin{matrix} H' \\ H' \end{matrix}\right\} O''$$

it is obvious that each or either of the atoms H′ can only be replaced by x' or $2_{,,}x$, thus:

$$\left.\begin{matrix} NO'_2 \\ NO'_2 \end{matrix}\right\} O''$$ nitric acid (anhydrous)

$$\left.\begin{matrix} K' \\ K' \end{matrix}\right\} O$$ potash

$$\left.\begin{matrix} 2_{,,}Hg \\ 2_{,,}Hg \end{matrix}\right\} O''$$ mercurous oxide

$$\left.\begin{matrix} NO'_2 \\ H' \end{matrix}\right\} O''$$ nitric acid

$$\left.\begin{matrix} NO'_2 \\ K' \end{matrix}\right\} O''$$ nitrate of potash

$$\left.\begin{matrix} H' \\ K' \end{matrix}\right\} O''$$ hydrate of potash

$$\left.\begin{matrix} NO'_2 \\ 2_{,,}Hg \end{matrix}\right\} O''$$ mercurous nitrate

$$\left.\begin{matrix} NO'_2 \\ Hg' \end{matrix}\right\} O''$$ mercuric nitrate.

Two atoms of water being taken as the type

$$\left.\begin{matrix} H' & H' \\ H' & H' \end{matrix}\right\} 2\ O''$$

One pair of H′ H′ being generally represented by x'', the other by x'', or $2\ x'$ or $4_{,,}\ x$, thus:

$$\left.\begin{matrix} SO'' \\ SO''_2 \end{matrix}\right\} 2\ O''$$ sulphuric acid (anhydrous)

$$\left.\begin{matrix} Sn'' \\ Sn'' \end{matrix}\right\} 2\ O''$$ stannic oxide or acid

$$\left.\begin{matrix} SO'' \\ Sn''_2 \end{matrix}\right\} 2\ O''$$ stannic sulphate

$$\left.\begin{matrix} SO''_2 \\ 2\ Sn' \end{matrix}\right\} 2\ O''$$ stannous sulphate

$$\left.\begin{matrix} 2\ NO'_2 \\ Sn'' \end{matrix}\right\} 2\ O''$$ stannic nitrate

$$\left.\begin{matrix} SO''_2 \\ 2\ K' \end{matrix}\right\} 2\ O''$$ potash sulphate

$$\left.\begin{matrix} SO''_2 \\ K'\,H' \end{matrix}\right\} 2\,O''$$ potash bisulphate

$$\left.\begin{matrix} SO''_2 \\ 2\,H' \end{matrix}\right\} 2\,O''$$ sulphuric acid

$$\left.\begin{matrix} SO''_2 \\ 2\,Hg' \end{matrix}\right\} 2\,O''$$ mercuric sulphate

$$\left.\begin{matrix} SO''_2 \\ 4_{,,}Hg \end{matrix}\right\} 2\,O''$$ mercurous sulphate.

Three atoms of water being taken as the type:

$$\left.\begin{matrix} H'\,H'\,H' \\ H'\,H'\,H' \end{matrix}\right\} O''_3$$

One tierce of H′ H′ H′ being generally represented by some substance having obvious tribasic tendencies, as x''', or xx''', or $x''+x'$; the other tierce being represented by x''', or xx''', or $x''+x'$, or $1\frac{1}{2}x''$, or $3\,x'$, or $6\,_{,,}x$.

In order to illustrate this series, I must make use of some tribasic acid, and avoiding the phosphoric acids for the present, avail myself of an organic acid, the citric.

The ordinary formula for hydrated critic acid is:

$$C_{12}\,H_5\,O_{11}+3\,HO$$
$$=C_{12}\,H_8\,O_{14},$$

and, by adopting the small equivalent for hydrogen,

$$=C_6\,H_8\,O_7$$
$$=\left.\begin{matrix} C_6\,H_5\,O_4 \\ 3\,H \end{matrix}\right\} 3\,O.$$

In the same manner the formula for hypothetical anhydrous citric acid is:

$$C_{12}\,H_5\,O_{11},$$

by adopting the small equivalent for hydrogen,

$$=C_{12}\,H_{10}\,O_{11}$$
$$=C_{12}\,H_{10}\,O_8+O_3$$
$$=\left.\begin{matrix} C_6\,H_5\,O_4 \\ C_6\,H_5\,O_4 \end{matrix}\right\} 3\,O,$$

in accordance with the previously used formulæ for the anhydrous acids.

Let Ci therefore stand for the compound $C_6\,H_5\,O_4$, and have a substitution value accorded to it equal to the value of 3 atoms of hydrogen, as in the following series:

$\left.\begin{matrix}Ci'''\\Ci'''\end{matrix}\right\}3\,O''$ citric acid (anhydrous)

$\left.\begin{matrix}Bi'''\\Bi'''\end{matrix}\right\}3\,O''$ bismuth teroxide

$\left.\begin{matrix}Fe'''_2\\Fe'''_2\end{matrix}\right\}3\,O''$ ferric oxide (sesquioxide)

$\left.\begin{matrix}Ci'''\\Fe'''_2\end{matrix}\right\}3\,O''$ ferric citrate

$\left.\begin{matrix}Ci'''\\1\tfrac{1}{2}\,Sn''\end{matrix}\right\}3\,O''$ stannic citrate?

$\left.\begin{matrix}Ci'''\\K'\,Sn''\end{matrix}\right\}3\,O''$ potassio-stannic citrate?

$\left.\begin{matrix}Ci'''\\3\,Ag'\end{matrix}\right\}3\,O''$ silver citrate

$\left.\begin{matrix}3\,NO'_2\\Bi'''\end{matrix}\right\}3\,O''$ bismuth nitrate

$\left.\begin{matrix}1\tfrac{1}{2}SO''_2\\Bi'''\end{matrix}\right\}3\,O''$ bismuth sulphate

$\left.\begin{matrix}Ci'''\\6\,,,Hg\end{matrix}\right\}3\,O''$ mercurous citrate

$\left.\begin{matrix}Ci'''\\3\,H'\end{matrix}\right\}3\,O''$ citric acid.

Four atoms of water being taken as a type,

$$\left.\begin{matrix}H'\,H'\,H'\,H'\\H'\,H'\,H'\,H'\end{matrix}\right\}4\,O''$$

without going into details concerning this group, it may suffice to cite alum as an example,

$$\left.\begin{matrix}2\,SO''_2\\K'\,Al'''_2\end{matrix}\right\}4\,O''.$$

All the salts hitherto brought forward are strictly neutral in composition: the formulæ are, however, equally applicable to basic and acid salts, as seen below:

$$\left.\begin{matrix}NO'_2\\Pb'\end{matrix}\right\}\,O''\quad\text{lead nitrate}$$

$$\left.\begin{matrix}Pb'\,NO'_2\\Pb'\,Pb'\end{matrix}\right\}2\,O''=\left.\begin{matrix}NO'_2\\3\,Pb'\end{matrix}\right\}2\,O''\quad\text{lead trisnitrate}$$

$$\left.\begin{matrix}Pb'\,NO'_2\,NO'_2\\Pb'\,Pb'\quad Pb'\end{matrix}\right\}3\,O''=\left.\begin{matrix}2\,NO'_2\\4\,Pb'\end{matrix}\right\}3\,O''\quad\text{lead dinitrate}$$

$$\left.\begin{matrix}IO'_2\\K'\end{matrix}\right\}\,O''\quad\text{potash iodate}$$

$$\left.\begin{matrix} IO'_2 \\ IO'_2 \end{matrix}\right.\left.\begin{matrix} IO'_2 \\ K'^2 \end{matrix}\right\} 2\,O'' = \left.\begin{matrix} 3\,IO'_2 \\ K'^2 \end{matrix}\right\} 2\,O''$$ potash teriodate

$$\left.\begin{matrix} IO'_2 \\ IO'_2 \end{matrix}\right.\left.\begin{matrix} IO'_2 \\ K'\,K \end{matrix}\right.\left.\begin{matrix} IO'_2 \\ K'^2 \end{matrix}\right\} 3\,O'' = \left.\begin{matrix} 4\,IO'_2 \\ 2\,K'^2 \end{matrix}\right\} 3\,O''$$ potash biniodate

A similar mode of notation is applicable to the salts of chromic acid, by which means, the bichromates and terchromates are made to appear as perfectly normal compounds.

The series of salts formed on the tartar emetic type are very clearly represented by these substitution formulæ, more especially when contrasted with salts of the alum type. The salts of both series agree in containing an atom of a monacid base, associated with an atom of a teracid base; those of the one class, however, being neutral and formed on the type of 4 atoms of water, those of the other being basic and formed on the type of 3 atoms of water.

Tartaric acid $= \left.\begin{matrix} C_4H_4O_4'' \\ 2\,H' \end{matrix}\right\} 2\,O'' = \left.\begin{matrix} T'' \\ 2\,H' \end{matrix}\right\} 2\,O''$ then we shall have

$\left.\begin{matrix} 2\,SO_2'' \\ K'\,Al'''_2 \end{matrix}\right\} 4\,O''$ common alum

$\left.\begin{matrix} K'\,SO''_2 \\ Al'''_2 \end{matrix}\right\} 3\,O''$ basic alum

$\left.\begin{matrix} 2\,T'' \\ K'\,Sb''' \end{matrix}\right\} 4\,O''$ neutral tartar emetic

$\left.\begin{matrix} K'\,T'' \\ Sb''' \end{matrix}\right\} 3\,O''$ tartar emetic

$\left.\begin{matrix} 2\,T'' \\ K'\,Fe'''_2 \end{matrix}\right\} 4\,O''$ neutral potash tartrate of iron

$\left.\begin{matrix} K'\,T'' \\ Fe'''_2 \end{matrix}\right\} 3\,O''$ basic potash tartrate of iron

$\left.\begin{matrix} 2\,T'' \\ K'\,B''' \end{matrix}\right\} 4\,O''$ tartarised borax

$\left.\begin{matrix} K'\,T'' \\ B''' \end{matrix}\right\} 3\,O''$ tartarised borax

I shall now endeavour to show the applicability of these views to certain series of salts, and for this purpose select the carbonates, sulphates, and phosphates, with their respective congeners.

And first, with regard to the carbonates, it will be seen that both carbonates and oxalates may be regarded as oxidised compounds of carbonic oxide with metals, but that in the former class the atom of carbonic oxide has a replaceable value equal to that of 2 atoms of hydrogen, whilst in the latter it has a value equal only to that of 1 atom of hydrogen. Similar considerations apply to the mesoxalates.

$\left.\begin{matrix} C\,O'' \\ C\,O'' \end{matrix}\right\} 2\,O''$ carbonic acid (anhydrous)

$\left.\begin{matrix} C\,O'' \\ 2\,H' \end{matrix}\right\} 2\,O''$ carbonic acid (hypothetical)

$\left.\begin{matrix} C\,O'' \\ 2\,K' \end{matrix}\right\} 2\,O''$ potash carbonate

$$\left.\begin{matrix} C\,O'' \\ K'\,H' \end{matrix}\right\} 2\,O''\ \text{potash bicarbonate}$$

$$\left.\begin{matrix} C\,O', C\,O' \\ 2\,H' \end{matrix}\right\} 2\,O''\ \text{or}\ \left.\begin{matrix} C_2\,O''_2 \\ 2\,H' \end{matrix}\right\} 2\,O''\ \text{oxalic acid}$$

$$\left.\begin{matrix} C\,O', C\,O' \\ 2\,K' \end{matrix}\right\} 2\,O''\ \text{or}\ \left.\begin{matrix} C_2\,O''_2 \\ 2\,K' \end{matrix}\right\} 2\,O''\ \text{potash oxalate}$$

$$\left.\begin{matrix} C_2\,O''_2 \\ K'\,H' \end{matrix}\right\} 2\,O''\ \text{potash binoxalate}$$

$$\left.\begin{matrix} 2\,C_2\,O''_2 \\ 3\,H', K' \end{matrix}\right\} 4\,O''\ \text{potash quadroxalate}$$

$$\left.\begin{matrix} C_3\,O''_3 \\ 2\,H' \end{matrix}\right\} 2\,O''\ \text{mesoxalic acid}$$

$$\left.\begin{matrix} C_3\,O''_3 \\ 2\,K' \end{matrix}\right\} 2\,O''\ \text{potash mesoxalate}$$

The action of heat on oxalate of potash is very clearly seen in these equational formulæ:

$$\left.\begin{matrix} C\,O', C, O' \\ 2\,K \end{matrix}\right\} 2\,O'' = \left.\begin{matrix} C\,O'' \\ 2\,K' \end{matrix}\right\} 2\,O'' + C\,O$$

also the action of heat on oxalate of nickel:

$$\left.\begin{matrix} C\,O', C\,O' \\ 2\,Ni' \end{matrix}\right\} 2\,O'' = \left.\begin{matrix} C\,O'' \\ C\,O'' \end{matrix}\right\} 2\,O'' + 2\,Ni$$

The following table represents in a similar manner the acids of sulphur and their salts:

$$\left.\begin{matrix} SO''_2 \\ SO''_2 \end{matrix}\right\} 2\,O''\ \text{sulphuric acid (anhydrous)}$$

$$\left.\begin{matrix} SO''_2 \\ 2\,H' \end{matrix}\right\} 2\,O''\ \text{sulphuric acid}$$

$$\left.\begin{matrix} SO''_2 \\ Na'\,H' \end{matrix}\right\} 2\,O''\ \text{soda bisulphate}$$

$$\left.\begin{matrix} SO''_2 \\ 2\,Na' \end{matrix}\right\} 2\,O''\ \text{soda sulphate}$$

$$\left.\begin{matrix} SO''_2 \\ 2\,Na' \end{matrix}\right\} O'' + S''\ \text{soda hyposulphite}$$

$$\left.\begin{matrix} SO''_2 \\ 2\,Na' \end{matrix}\right\} 2\,S''\ \text{hyposulphite of sulphide of sodium}$$

$$\left.\begin{matrix} SO''_2 \\ 2\,Na' \end{matrix}\right\} O'' + 2\,NO'\ \text{soda nitrosulphate}$$

$\left.\begin{matrix} SO'_2 \\ 2\,Na' \end{matrix}\right\}\begin{matrix} SO'_2 \\ \end{matrix}\Big\}2\,O''$ or $\left.\begin{matrix} S_2\,O''_4 \\ 2\,Na' \end{matrix}\right\}2\,O''$ soda hyposulphate

$\left.\begin{matrix} SO'_2 \\ 2\,H' \end{matrix}\right\}\begin{matrix} SO_2 \\ \end{matrix}\Big\}2\,O''$ or $\left.\begin{matrix} S_2\,O''_4 \\ 2\,H' \end{matrix}\right\}2\,O''$ hyposulphuric acid

$\left.\begin{matrix} SO'' \\ SO'' \end{matrix}\right\}2\,O''$ sulphurous acid

$\left.\begin{matrix} SO'' \\ Na'\,H' \end{matrix}\right\}2\,O''$ soda bisulphite

$\left.\begin{matrix} SO'' \\ 2\,Na' \end{matrix}\right\}2\,O''$ soda sulphite

The relations of the hyposulphates to the sulphates are in this way made very apparent. Hyposulphates stand to the sulphates in a position similar to that which the oxalates occupy with regard to the carbonates; and here likewise the action of heat is very clearly pourtrayed:

$$\left.\begin{matrix} SO'_2 \\ 2\,Na' \end{matrix}\right\}\begin{matrix} SO'_2 \\ \end{matrix}\Big\}2\,O'' = \left.\begin{matrix} SO''_2 \\ 2\,Na' \end{matrix}\right\}2\,O'' + SO_2$$

In fact, the hyposulphates are sulphates into the constitution of which another atom of sulphurous acid has been forced.

With regard to the sulphites, a radical SO is made use of, which is not known to have any real existence. That such a substance should, however, exist in compounds, is not by any means improbable when we consider the analogies of the sulphites, selenites, and carbonates, as pointed out by Muspratt, and as seen below:

CO	SeO	
CO_2	SeO_2	SO_2
	SeO_3	SO_3

To proceed to a consideration of the acids of phosphorus and their salts, I am desirous of discussing the relations of this series somewhat more fully than those of the preceding ones, and shall venture to premise a few general remarks. It appears to me, that chemists have usually been too prone to regard all irregularities in the properties of bodies, as special differences between such and other more orthodox substances; whereas, a more deliberate examination of the subject would show that most of these apparent differences in kind, were in reality only differences in degree. I think it may be taken as a rule, that every obvious abnormality in the constitution or properties of any particular body, is but an exaggerated condition of quality which exists latent in other bodies;

so that while these abnormal bodies are constantly, and under every variety of circumstance, obtruding their peculiarities upon our notice, it is only by intentional search, and under the most favourable conditions, that the same characters will be found to obtain, though in a less marked degree, in other more normal bodies.

Moreover, we are oftentimes apt to overlook broad features of resemblance between different substances, from the accidental circumstance of such substances having been originally regarded in different aspects; the similitude is, however, rendered at once apparent by simply altering our point of view.

Thus the phosphoric acid is usually considered as peculiar, inasmuch as its saturating power varies remarkably in different instances. Now I believe that by changing our point of view, this property will prove to be not of a special kind, but a special illustration of a general law, prevailing, though to a much lower degree, in other compounds. My object, then, in the succeeding remarks, is to point out the method of representing the phosphates in accordance with the previously used substitution formulæ, and at the same time to show that their so-called peculiarities are manifested, though to a much less extent, in the salts of many other acids, certainly in the chromates, borates, iodates, and sulphates.

In the first instance, confining myself to considerations connected with the common phosphates and the meta-phosphates, I was desirous to know whether the meta-phosphate ought to be regarded as the normal salt, and the common phosphate as a salt containing an excess of base; or whether the common phosphate was the normal salt, and the meta-phosphate a salt containing an excess of acid. From thinking over the modes of formation and general habitudes of the salts, I was induced to adopt the latter assumption, and to represent ordinary terhydrated phosphoric acid as

$$\left.\begin{matrix} PO''' \\ 3\,H' \end{matrix}\right\} 3\,O''$$

any tribasic phosphate

$$\left.\begin{matrix} PO''' \\ x'\ y'\ z' \end{matrix}\right\} 3\,O''$$

and the anhydrous acid as:

$$\left.\begin{matrix} PO''' \\ PO''' \end{matrix}\right\} 3\,O''$$

compounds formed on the type of three atoms of water.

Now, if one such atom of a tribasic phosphate containing three

atoms of fixed base were fused with one atom of anhydrous phosphoric acid, one atom of meta-phosphate would result: thus

$$\left.\begin{matrix} PO''' & PO''' \\ 3\,K' & PO''' \end{matrix}\right\} 6\,O''$$

and the meta-phosphate would be considered as a common phosphate combined with anhydrous phosphoric acid, in the same manner that bichromate of potash is regarded as a combination of neutral chromate of potash with anhydrous chromic acid; biniodate of potash, a combination of neutral iodate with anhydrous iodic; biborate, a combination of neutral borate with anhydrous boric; bisulphate, as a combination of neutral sulphate with anhydrous sulphuric acid, &c.* Now I believe that this analogy will be found to be an analogy proper, having a real existence in fact, and being sufficient to warrant our removing the phosphates from their present isolated position, and to our associating them with other anhydrous acid salts, the number of which I have no doubt might be greatly increased.

There is no difficulty whatever in making the salts agree perfectly well as regards their formulæ, as seen on next page; chromic acid being represented as bibasic, its bibasity being inferred from its analogy to sulphuric acid, and from the vapour-density of its oxychloride.

Wurtz's views of the constitution of the hypophosphites and phosphites, accord extremely well with these substitution-formulæ, the relations of the former to the metaphosphates, and of the latter to the pyrophosphates, being most fully preserved.

$$\left.\begin{matrix} PO''' \\ K' \end{matrix}\right\} 2\,O''$$

Metaphosphate.

$$\left.\begin{matrix} PH'''_2 \\ K' \end{matrix}\right\} 2\,O''$$

Hypophosphite.

$$\left.\begin{matrix} 2\,PO''' \\ 4\,K' \end{matrix}\right\} 5\,O''$$

Pyrophosphate.

$$\left.\begin{matrix} PO''' & PH'''_2 \\ 4\,K' \end{matrix}\right\} 5\,O''$$

Phosphite.

It becomes a question, however, whether the phosphite might not be better represented as a homologue of the common phosphate,

$$\left.\begin{matrix} PO''' \\ 2\,K', H' \end{matrix}\right\} 3\,O''$$

Phosphate of potash, ordinary.

$$\left.\begin{matrix} P'' \\ 2\,K', H' \end{matrix}\right\} 3\,O''$$

Phosphite of potash, ordinary.

* The bisulphate to which I refer, is that described by Jacquelain, having the composition $KO\,SO_3, SO_3$, analogous to the Nordhausen acid $HO\,SO_3, SO_3$.

$\left.\begin{matrix} IO'_2 \\ IO'_2 \end{matrix}\right\}$ O″ iodic acid

$\left.\begin{matrix} IO'_2 \\ K' \end{matrix}\right\}$ O″ potash iodate

By combining 1 atom of each of the above compounds, we have:

$\left.\begin{matrix} IO'_2 & IO'_2 \\ K' & IO'_2 \end{matrix}\right\}$ 2 O″ potash teriodate

$= \left.\begin{matrix} 3\ IO'_2 \\ K' \end{matrix}\right\}$ 2 O″

As an intermediate compound between the iodate and teriodate, we have the biniodate:

$\left.\begin{matrix} IO'_2 & IO'_2 & IO'_2 \\ K' & K' & IO'_2 \end{matrix}\right\}$ 3 O″

$= \left.\begin{matrix} 4\ IO'_2 \\ 2\ K' \end{matrix}\right\}$ 3 O″

$\left.\begin{matrix} Cr_2O''_2 \\ Cr_2O''_2 \end{matrix}\right\}$ 2 O″ chromic acid

$\left.\begin{matrix} Cr_2O''_2 \\ 2\ K' \end{matrix}\right\}$ 2 O″ potash chromate

By combining 1 atom of each of the above compounds, we have:

$\left.\begin{matrix} Cr_2O''_2 & Cr_2O''_2 \\ 2\ K' & Cr_2O''_2 \end{matrix}\right\}$ 4O″ potash terchromate

$= \left.\begin{matrix} 3\ Cr_2O''_2 \\ 2\ K \end{matrix}\right\}$ 4O″

As an intermediate compound between the chromate and terchromate, we have the bichromate:

$\left.\begin{matrix} Cr_2O''_2 & Cr_2O''_2 & Cr_2O''_2 \\ 2\ K' & 2\ K' & Cr_2O''_2 \end{matrix}\right\}$ 6O″

$= \left.\begin{matrix} 2\ Cr_2O''_2 \\ 2\ K' \end{matrix}\right\}$ 3O″

$\left.\begin{matrix} PO''' \\ PO''' \end{matrix}\right\}$ 3 O″ phosphoric acid

$\left.\begin{matrix} PO''' \\ 3\ K' \end{matrix}\right\}$ 3 O″ potash tribasic phosphate

By combining 1 atom of each of the above compounds, we have:

$\left.\begin{matrix} PO''' & PO''' \\ 3\ K' & PO''' \end{matrix}\right\}$ 6 O″ metaphosphate of potash

$= \left.\begin{matrix} PO''' \\ K' \end{matrix}\right\}$ 2 O″

As an intermediate compound between the common and the metaphosphate we have the pyrophosphate:

$\left.\begin{matrix} PO''' & PO''' \\ 3\ K' & K' \end{matrix}\right\}$ 5 O″

$= \left.\begin{matrix} 2\ PO''' \\ 4\ K' \end{matrix}\right\}$ 5 O″

The exact homologue of the bichromates and biniodates is to be found in one of Fleitmann and Henneberg's salts.

By this means we should make use of three phosphorus radicals,

$$PH_2,\ P,\ \text{and}\ PO,$$

each having a replaceable value equal to that of 3 atoms of hydrogen.*

The mode I have adopted for expressing the pyrophosphates represents most clearly the constitution of certain double pyrophosphates, one of which Mr. Graham has noticed as being inimical to Fleitmann and Henneberg's views.

$$\left.\begin{matrix}2\,PO''' \\ 3\,Na',\ Cu'\end{matrix}\right\}5\,O'',\ \text{new formula,}$$

$$3\,(2\,NaO,\ PO_5) + 2\,CuO,\ PO_5,\ \text{old formula,}$$

for the double pyrophosphate of soda and copper.

Having thus pointed out the almost complete correspondence of the formulæ of the above salts, I proceed to discuss the correspondence of their properties, and I trust I shall be able to show, that the different members of the series partake of a common character, and that such differences as exist among them are not differences of kind, but only modifications of general properties, depending for the most part upon ascertainable modifying conditi ons.

If any of the above anhydrous acid salts be dissolved in an

* Since reading the above paper, Dr. Williamson has pointed out to me, that by making use of another phosphorized radical PO_2, the phosphates may be represented in a manner different to the above This difference in the formulæ may perhaps explain the constitution of the two principal classes of metaphosphates and their derivatives.

Metaphosphates:

$$\left.\begin{matrix}PO'_2 \\ H'\end{matrix}\right\}O''\quad\text{or}\quad\left.\begin{matrix}PO''' \\ H'\end{matrix}\right\}2\,O''$$

Pyrophosphates:

$$\left.\begin{matrix}2\,PO'_2 \\ 4\,H'\end{matrix}\right\}3\,O''\ \text{or}\ \left.\begin{matrix}PO'_2\,PO''' \\ 4\,H'\end{matrix}\right\}4\,O''\quad\text{or}\quad\left.\begin{matrix}2\,PO''' \\ 4\,H'\end{matrix}\right\}5\,O''$$

Common phosphates:

$$\left.\begin{matrix}PO'_2 \\ 3\,H'\end{matrix}\right\}2\,O''\ \text{or}\ \left.\begin{matrix}PO''' \\ 3\,H'\end{matrix}\right\}3\,O''$$

It is to be observed that Dr. Williamson's view makes the metaphosphates analogous to the nitrates:

$$\left.\begin{matrix}NO'_2 \\ Na'\end{matrix}\right\}O''\qquad\left.\begin{matrix}PO'_2 \\ Na'\end{matrix}\right\}O''$$

Nitrate and metaphosphate of soda respectively.

excess of cold water, one of two circumstances will take place; either the free acid will remain attached to the salt and not take up basic water, as is the case with boric and chromic acids, or the free acid will unite with basic water, gradually, as is the case with the phosphoric acid, or more rapidly, as is the case with the sulphuric.

That the free boric and chromic acids should behave as they do, is easily explicable, when we consider that neither of them forms a definite basic hydrate. That the free anhydrous sulphuric acid should take up water rapidly, is what we might expect, from its powerful affinity for water; that the free anhydrous phosphoric acid should not take up water so rapidly as does the sulphuric, is accounted for readily, when we consider the different conditions which determined the existences of the salts respectively containing them.

If, however, the above salts be dissolved in boiling water, the anhydrous sulphuric and phosphoric acids alike take up water rapidly, so as to form the normal salts. If, moreover, a solution of potash or soda be used instead of water, the free anhydrous boric, chromic, sulphuric, and phosphoric acids alike take up the added base, to form normal salts: the boric, however, from the feebleness of its acid properties, by which it is obviously fitted to act as an acid adjunct, does not manifest this action to the same degree as do the others.

When common phosphoric acid is heated to a certain point, it loses a definite amount of water, and metaphosphoric acid results from the combination of the nascent anhydrous phosphoric acid with some of the unaltered common acid; sulphuric acid cannot, however, be changed in this manner, because the anhydrous acid being volatile, the physical action of heat is not opposed to the affinities, as in the preceding case.

The similar blowpipe properties of phosphorus-salt and borax are explained by this view of their similar constitution. In each instance we have free anhydrous acid at an intense heat, extremely fixed, and in a liquid condition; when a metallic salt or oxide is added, combination takes place as a matter of course, and the borate or phosphate of metal unites with or dissolves in the borate or phosphate of alkali. But if we employ either normal or basic borates or phosphates, we do do not get these coloured beads, or at any rate but very imperfect ones, such action as does occur being probably due to the partial replacement of the volatile soda by the fixed metallic oxide.

A further parallelism between the phosphates and chromates is seen below.

The substance $\left.\begin{matrix}Cr_2O''\\2\,K'^2\end{matrix}\right\}$ 2 O″ is unaltered at a red heat.

the substance $\left.\begin{matrix}Cr_2O''\\Cr_2O''_2\end{matrix}\right\}$ 2 O″ is decomposed at a red heat—if

the substance $\begin{matrix}Cr_2O''\\2\,K'^2\end{matrix}$ $\left.\begin{matrix}Cr_2O''\\Cr_2O''_2\end{matrix}\right\}$ 4 O″ be heated to redness,

the $\left.\begin{matrix}Cr_2O''\\2\,K'^2\end{matrix}\right\}$ 2 O″ remains unaltered,

while the $\left.\begin{matrix}Cr_2O''\\Cr_2O''_2\end{matrix}\right\}$ 2 O″ becomes decomposed.

The substances $\left.\begin{matrix}PO'''\\3\,K'\end{matrix}\right\}$ 3 O″

and $\left.\begin{matrix}PO'''\\PO'''\end{matrix}\right\}$ 3 O″

are both unaltered by heat alone, but while

the substance $\left.\begin{matrix}PO'''\\3\,K'\end{matrix}\right\}$ 3 O″ is unaltered at a red heat in the presence of charcoal,

the substance $\left.\begin{matrix}PO'''\\PO'''\end{matrix}\right\}$ 3 O″ is decomposed under similar conditions. If then

the substance $\begin{matrix}P'''O\\3\,K'\end{matrix}$ $\left.\begin{matrix}PO'''\\PO'''\end{matrix}\right\}$ 6 O″ be mixed with charcoal and heated to redness,

the substance $\left.\begin{matrix}PO'''\\3\,K'\end{matrix}\right\}$ 3 O″ remains unaltered, while

the substance $\left.\begin{matrix}PO'''\\PO'''\end{matrix}\right\}$ 3 O″ becomes decomposed; or, in other words, when a metaphosphate is mixed with charcoal and heated to redness, a common phosphate, with 3 atoms of fixed base, results; in proof of which, I offer the following experiments.

If a bead of metaphosphate of soda be heated with charcoal in the reducing-flame of the blowpipe, and then be dissolved in water, the solution will give a yellow precipitate with nitrate of silver.

If the metaphosphate be intimately mixed with an excess of charcoal (free from organic matter, as procured by the incineration of sugar), and the mixture be put into a crucible and kept at a full red heat for some time, inflammable vapours, smelling of phos-

phorus, are given off; fusion does not take place, but the black powder, when heated with water, affords a solution which gives a yellow precipitate with nitrate of silver.

The solution, when evaporated to dryness and ignited, leaves a semicrystalline mass, which by analysis is shown to have the following composition:

	Calculation.	Found.	Found.
3 NaO	56·73		
PO_5	43·27	44·56	44·31

These are the two best results of several analyses. The salt had a powerful alkaline reaction, and absorbed carbonic acid with considerable rapidity; when too intense a heat was employed, some of the phosphate was converted into phosphuret.

These analogies are, I think, sufficient to warrant the views which I have put forward with reference to the phosphates.* At the commencement of my endeavours to apply the substitution formulæ to this class of salts, I experienced considerable difficulty, and was at one time induced to adopt an opinion which I subsequently found had been proposed by Gerhardt, viz., that the metaphosphates were the normal salts, and the pyrophosphates and common phosphates modifications of ordinary basic salts.

I was inclined to this view from a consideration of certain resemblances between the sulphuric and phosphoric acids as commonly represented, and being thereby led to one or two experiments, which, though simple, are not without interest, I venture to allude to them; especially as the results, though at first sight inimical to the views I have above detailed, are quite capable of being explained by them.

Any dilute sulphuric acid evaporated *in vacuo*, at a temperature of 212° F., becomes SO_3, 3 HO.

By heating the above to a temperature a little above 400° F., we have

SO_3 2 HO.

A solution of common phosphoric acid, similarly treated, leaves the compound $P O_5$, 3 HO.

By heating the above to a temperature of 415° F., we have

PO_5 2 HO.

* If Fremy's experiments on the tartaric, tartrelic, and tartralic acids should be ultimately confirmed, that series would afford an abundant illustration, both as regards formulæ, formation and properties, of the correctness of the above mode of representing the meta- and pyrophosphates, viz., as salts containing an excess of anhydrous acid. I was unwilling, however, to draw deductions from results which are still *sub judice*.

By a further increment of temperature, we have

SO_3 HO.

By a further increment of temperature, we have

PO_5 HO.

Again, subsulphate of mercury and yellow phosphate of silver receive similar formulæ:

SO_3 3HgO $\qquad\qquad$ PO_5 3AgO.

When decomposed by sulphuretted hydrogen, they yield similar acids:

$$SO_3,\ 3\ HgO + 3\ HS = SO_3,\ 3\ HO + 3\ HgS$$
$$PO_5\ 3\ AgO + 3\ HS = PO_5\ 3\ HO + 3\ AgS$$

But the salts SO_3 3 Hg O and PO_5 3 Ag O are made in very different ways. Being struck with the above analogies, I endeavoured to make similar basic sulphates and phosphates by one and the same method.

For this purpose, I made use of the tribasic acetate of lead, conceiving that by adding a solution of this salt to solutions of sulphate and metaphosphate of soda respectively, I should get formed, by double decomposition, tribasic sulphates and phosphates of lead, as represented below:

$$\bar{A},\ 3\ PbO + NaO,\ SO_3 = 3\ PbO,\ SO_3 + NaO,\ A$$
$$\bar{A},\ 3\ PbO + NaO,\ PO_5 = 3\ PbO,\ PO_5 + NaO,\ A$$

that is to say, that the lead phosphate made by decomposing metaphosphate of soda by tribasic acetate of lead, would have the same composition as the lead phosphate made by decomposing common phosphate of soda by neutral acetate of lead. Would it, however, yield the same result when decomposed by sulphuretted hydrogen? would it prove to be a metaphosphate of lead + 2 atoms of oxide of lead, and consequently yield metaphosphoric acid? or would it prove to be the real tribasic phosphate of lead, yielding the common phosphoric acid? I will detail an experiment. Metaphosphate of soda was prepared by ignition of microcosmic salt. The clear glass was broken up in a mortar and dissolved in ice-cold water. Into this solution was filtered an ice-cold solution of tribasic acetate of lead, until the lead-salt remained slightly in excess; the whole was well agitated, thrown on a filter, and washed with ice-cold water. The first portions of the precipitate produced by the lead-salt were redissolved in the excess of metaphosphate; the precipitate permanently resulting had a granular appearance and was very easily washed; the washed precipitate

was mixed with water and decomposed by sulphuretted hydrogen. The whole was allowed to stand in an evaporating dish for about twenty hours, to get rid of the excess of sulphuretted hydrogen. It was then filtered, and the acid filtrate being rendered slightly ammoniacal, nitrate of silver was added, and an abundant yellow flocculent precipitate took place. The colour was not so deep as that produced by adding nitrate of silver to common phosphate of soda, but still it was decidedly yellow, quite as much so as the rind of a lemon. This experiment was repeated several times with slight modifications in its mode of performance; sometimes the lead-salt was added to the metaphosphate, sometimes the metaphosphate to the lead-salt; sometimes the one was in excess, sometimes the other; sometimes the crystalline, and sometimes the glassy metaphosphate was employed. In a few instances, to avoid waiting for the removal of the excess of sulphuretted hydrogen, the gas was only passed through a portion of the suspended precipitate, and when that portion was thoroughly decomposed, the remainder added little by little, agitating between each addition, until all odour was removed, then filtering and applying the silver-test at once. In every trial, the above-described yellow precipitate was obtained: from the same filtrate the appearance of the precipitate occasionally varied considerably, according to accidental circumstances connected with the precipitation, &c. In no case was metaphosphoric acid entirely absent, although sometimes its amount was but very small. A portion of the phosphate of lead with which the above-detailed experiment was made, was partly analyzed.

9·48 grs. of the thoroughly dried precipitate yielded 7·304 grs. of oxide of lead, whereas to have been a real tribasic phosphate it ought to have contained 7·811 grs.

A specimen of basic sulphate of lead, prepared in a similar manner, was examined.

9·69 grs. of the thoroughly dried precipitate yielded 8·35 grs. of oxide of lead, whereas to have been a real tribasic sulphate it should have yielded 8·66 grs.

These results, at the first glance, seem in favour of the idea that the tribasic phosphates should be represented as basic salts; but by looking at the subject from another point of view, we shall see nothing extraordinary in the fact of an acid salt taking up base to become a normal salt, especially when, as in the preceding instance, the base is presented in a sort of nascent state.

There are, however, undoubtedly certain resemblances between common phosphates containing 3 atoms of a powerful base, and

ordinary basic salts, in the same manner as the normal salts of teroxides approximate in their characters to acid salts, and obviously for a similar reason—viz., that in the one case the tribasic acid is incapable of entirely neutralizing the 3 atoms of a powerful base, and in the other the teroxide is incapable of saturating the 3 atoms of a powerful acid; and it is probably this incapacity for thoroughly neutralizing the normal proportions of a powerful base that renders the phosphoric acid, like the boric, eminently fitted to act as an acid adjunct.

With reference to the constitution of such bodies as common salt, muriatic acid, &c., let $\left.\begin{matrix}H'\\H'\end{matrix}\right\}O''$ represent water. If we replace the oxygen by chlorine, we shall have the formula $\left.\begin{matrix}H'\\H'\end{matrix}\right\}Cl'$; but whereas the symbol of water is, so to speak, reduced to its lowest terms, the symbol of hydrochloric acid is obviously capable of division into 2 equivalents of H′Cl′, so that in reality 2 atoms of hydrochloric acid are required to represent 1 atom of water, the reason being that in the latter case the separable equivalents of hydrogen are held together by the indivisible oxygen. But, on the other hand, we may represent common salt and other similar bodies as analogues of the double atom of hydrogen. If in water we suppose the atom of oxygen to be replaced by hydrogen, we get the formula $\left.\begin{matrix}H'\\H'\end{matrix}\right\}\left.\begin{matrix}H'\\H'\end{matrix}\right.$ precisely analogous to $\left.\begin{matrix}H'\\H'\end{matrix}\right\}\left.\begin{matrix}Cl'\\Cl'\end{matrix}\right.$ and $\left.\begin{matrix}K'\\K'\end{matrix}\right\}\left.\begin{matrix}Cl'\\Cl'\end{matrix}\right.$; and as each of these last ones splits itself into 2 equivalents of chloride, H′Cl′ or K′Cl′, so does the other separate into 2 equivalents of hydride, H′ H′, any further division being opposed by the antipolar relations of the atoms. This explains how it is that in salts we not unfrequently find such compounds as KCl substituted for the hydrogen, as seen below:

$\left.\begin{matrix}H'\\H'\end{matrix}\right.\quad\left.\begin{matrix}H'\\H'\end{matrix}\right\}O''$ water

$\left.\begin{matrix}Cl'\\K'\end{matrix}\right.\quad\left.\begin{matrix}Cl'\\K'\end{matrix}\right\}O''$ hypochlorite of potash

$\left.\begin{matrix}NO'_2\\K'\end{matrix}\right.\quad\left.\begin{matrix}NO'_2\\K'\end{matrix}\right\}O''$ nitrate of potash

$\left.\begin{matrix}Cy'\\K'\end{matrix}\right.\quad\left.\begin{matrix}Cy'\\K'\end{matrix}\right\}O''$ cyanate of potash

$\left.\begin{matrix}Cy'\\K'\end{matrix}\right.\quad\left.\begin{matrix}Cy'\\K'\end{matrix}\right\}S''$ sulphocyanate of potash

According to the above table, the salts on the right hand column are considered as oxides or sulphides of independent self-existing compounds, and I believe that such is really a correct mode of representing them; the second instance is, perhaps, more liable to exception than the others. My object, however, is rather to show how a very large number of bodies may be looked upon from a single point of view, than to prove that in every instance this point of view is necessarily the best one from which each particular object can be regarded.

To advert briefly to some of the most important advantages accruing from this view of the constitution of salts, and, in the first place, to its almost unlimited applicability. By the adoption of an extremely simple type, bodies of the most different properties are brought together under a common formula; such is its comprehensiveness, that salts previously considered most heterodox in their composition are included with as much facility as are their more normal congeners.

It comprises equally well the compounds derived from organic and from inorganic chemical action, and assimilates them to one another in a most marked degree.

If it complicates the formulæ of a few salts, it simplifies the representation of very many, as seen particularly in the cases of the citrates, the alums, and sulphates; its few complications, moreover, are rather apparent than real, and would obtain to nearly an equal degree in the old modes of writing, were the atom of hydrogen and its analogues doubled.

The type being neutral in composition, it follows that all the various substances formed on that type are likewise neutral in composition; a consideration of some importance as illustrating the simple deductions which proceed from the view. It explains clearly the mode of formation of normal salts. It used to be considered a strong argument in favour of the binary theory of salts, that it accounted satisfactorily for the well-known fact, that when an atom of base united with a monobasic acid to form a normal salt, it invariably required as many atoms of acid as itself contained atoms of oxygen; but by representing salts, in accordance with the above-detailed views, as substitution-products, more especially when the exponential notation is adopted, this fact will be better explained than even by the binary theory, and will then appear as a particular illustration of a general law, and as a necessary consequence of the substitutions connected with the formation of the salt: thus

$\left.\begin{matrix}K'\\K'\end{matrix}\right\}O$, K having a single representative value, is replaced by 1 atom of NO_2 to form the salt, $\left.\begin{matrix}NO'_2\\K'\end{matrix}\right\}O$,

$\left.\begin{matrix}Sn''\\Sn''\end{matrix}\right\}O_2$, Sn having here a double representative value, is replaced by 2 atoms of NO'_2 to form the salt $\left.\begin{matrix}2\,NO'_2\\Sn''\end{matrix}\right\}O_2'$

$\left.\begin{matrix}Bi'''\\Bi'''\end{matrix}\right\}O_3$, Bi having a treble representative value, is replaced by 3 atoms of NO_2 to form the salt $\left.\begin{matrix}3\,NO'_2\\Bi'''\end{matrix}\right\}O_3$, and so on.

In common with the binary theory, it accords but one explanation of the ordinary action of easily oxydizable metals upon acid solutions, thus:

$$\begin{matrix}H'\\Cl'\end{matrix} + Zn' = \begin{matrix}Zn'\\Cl'\end{matrix} + H'$$

$$\left.\begin{matrix}SO''\\2\,H'\end{matrix}\right\}2\,O'' + 2\,Zn' = \left.\begin{matrix}SO''\\2\,Zn'\end{matrix}\right\}2\,O'' + 2\,H'$$

the result at any rate being that the zinc in each case simply replaces the hydrogen.

And lastly, these formulæ are quite in accordance with the atomic theory, in which respect they differ most remarkably from Gerhardt's. By establishing a difference to the eye between the atom of a body and its equivalent or substitution value, we gain a clearer idea of the precise meaning of these respective terms. Thus the atom of bismuth is marked with three dashes, Bi‴, to indicate that the atom of bismuth replaces or is equivalent to three atoms of hydrogen, and so on. Gerhardt, on the other hand, writes $\left.\begin{matrix}bi\\Cl\end{matrix}\right\}$ in which bi is supposed to be $\frac{1}{3}$ of Bi.

Such then are my reasons for applying the substitution formulæ to the inorganic chemical products. I do not consider it at all necessary to the integrity of these views, that the subordinate compounds indicated in the formulæ should in all cases be considered to have an actual, much more an independent existence. I make use of them only as representing, among the many possible arrangements of the elements, the ones which I consider illustrate the most probable action of the affinities concurring in the production of the salt. Even were it otherwise, however, I do not think that

those chemists who consider silicate of soda to contain ready formed the compound Si O_4 ($NaSiO_4$) and that the three phosphoric acids contain respectively such different, and out-of-the-way compounds, as P O_6, P O_7, and P O_8, need demur at such simple subordinate compounds as I have ventured to introduce.

II.—*On the Platino-tersulphocyanides and the Platino-bisulphocyanides, two new series of salts, and their decompositions.*

By George Bowdler Buckton, F.L.S.

Although the salts of platinum have been pretty closely studied by chemists, and are perhaps found to be more numerous than those of any other metal, there is some room for surprise that scarcely any attention has been paid to their action upon sulphocyanogen compounds. The only notice I have been able to find of a sulphocyanide of platinum, is that made by Grotthus, and quoted by Brande, stating it to occur as a bulky flocculent precipitate of a yellow colour, soluble in acids and in solutions of chloride of potassium and sodium, but thrown down again from these solutions by alcohol. Hitherto, I have not met with a substance answering these properties, unless it should prove to be identical with that last described in this paper.

The addition of bichloride of platinum to a cold solution of sulphocyanide of potassium alone gives rise to the ordinary double salt, chloroplatinate of potassium, with disengagement of hydrosulphocyanic acid. If on the other hand, a strong solution of sulphocyanide of potassium be previously heated to 70° or 80° C., there is no precipitation, but the liquid changes to a deep port-wine-red colour, accompanied with a rise in temperature. On standing, this solution deposits a multitude of brilliant red or gold-coloured plates, which are very soluble in hot water. By this process, much waste of sulphocyanide of potassium is unavoidable, from the presence of free hydrochloric acid, which also decomposes the new compound into a brown flocculent precipitate, if the temperature rises above a certain point.

A more profitable operation consists in dissolving in a moderate quantity of water, five parts of pure sulphocyanide of potassium, weighed in an anhydrous state, which is best obtained by fusion. Four parts of dry chloroplatinate of potassium are then added by degrees to the solution, combination with which may be promoted by

a heat regulated below the boiling point. A deficiency of the sulphocyanide must be carefully avoided, as in such a case the above-mentioned brown product is an invariable result, rendering the purification of the crystals exceedingly difficult. After filtering the hot liquid, it is set apart to cool, when the new salt is deposited in beautiful and regular hexagons, often of a large size. To remove traces of chloride of potassium, one product of the reaction, the crystals may be redissolved in boiling alcohol, and passed through a filter surrounded with hot water, a necessary precaution to prevent obstruction from a too rapid crystallization. The solid salt dissolves in 12 parts of water at 60° C., but is far more soluble in boiling water, and still more so in hot alcohol. The crystals, which are of a deep carmine red, belong to the rhombohedral or three and one-membered system. From the alcoholic solution they often take the form of double six-sided pyramids, united base to base with apices truncated; but the aqueous solution usually furnishes hexagonal plates.

With access of air, this substance ignites at a very gentle heat, with a blue sulphurous flame and peculiar odour. A red heat resolves it into sulphocyanide of potassium, gaseous products, and reduced platinum. In common with all the soluble salts to be described, it has an exceedingly nauseous taste, and the colour is so intense, that one drop of a saturated solution will give a distinct yellow tinge to a gallon of water.

A pure solution does not strike a blood-red colour with sesquichloride of iron; but such a mixture becomes nearly black and opaque on heating, from the formation of a substance in heavy lustrous grains. Caustic potassa converts the red salt into a red gelatinous mass, without evolution of ammonia, which, however, is freely disengaged on ignition with soda-lime. Acted on by hydrosulphuric acid, the salt is resolved into hydrosulphocyanic acid, sulphocyanide of potassium, and bisulphide of platinum. It is also decomposed by concentrated sulphuric and hydrochloric acids. The action of nitric acid will be afterwards referred to.

The dry salt is quite permanent at ordinary temperatures; but from its inability to bear a high degree of heat without decomposition, most of the compounds to be described were dried *in vacuo* over sulphuric acid, previous to analysis.

The potassium was separated by precipitating the new acid with nitrate of silver. After removing the excess by hydrochloric acid, the alkali was weighed in the form of chloroplatinate of potassium.

The platinum was determined by igniting the bisulphide, precipitated by sulphide of ammonium.

The carbon was estimated by burning the substance in a stream of air and oxygen, observing the usual precautions for absorbing traces of nitrous and sulphurous acids.

And here I may be allowed to bear a grateful testimony to the readiness and convenience in determinations of this kind, afforded by the gas-furnace for organic analysis, lately constructed and described by Dr. Hofmann. From the abrupt decomposition and presence of both sulphur and nitrogen in the substances to be noticed, their determinations may be said to present more than usual difficulty. Attention, however, to slow burning is all that is necessary in these cases, to procure accurate results. By the simple addition of another tube and piston, nitrogen determinations may be also conducted with great neatness and accuracy.

The sulphur was determined by oxydizing the substance with chlorate of potassa and hydrochloric acid, assisted by gentle heat. Sufficient boiling water was then added to hold in solution any chloroplatinate that might be formed, and the precipitate from chloride of barium was filtered off whilst hot. This method was found to obviate the tedious washings which are necessary when fuming nitric acid or a nitrate is employed. Its substitution is strongly recommended in the analysis of volatile sulphuretted compounds.

I.	0·7554	grm. of substance	gave	0·6030	grm. of	chloroplatinate of potassium.
I.	0·7050	„	„	0·2230	„	platinum.
II.	0·9132	„	„	0·2876	„	platinum.
III.	0·5980	„	„	0·1900	„	platinum.
I.	1·0900	„	„	0·4582	„	carbonic acid.
II.	1·0160	„	„	0·4390	„	carbonic acid.
I.	0·7264	„	„	1·5705	„	chloroplatinate of ammonium.
II.	1·0044	„	„	2·1888	„	chloroplatinate of ammonium.
III.	0·6628	„	„	1·4492	„	chloroplatinate of ammonium.
I.	0·5628	„	„	1·2600	„	sulphate of baryta.
II.	0·4030	„	„	0·9096	„	sulphate of baryta.

The corresponding percentages to these numbers are :

	I.	II.	III.
Potassium	12·73	—	—
Platinum	31·64	31·49	31·77
Carbon	11.64	11·78	—
Nitrogen	13·54	13·56	13·66
Sulphur	30·70	30·96	—

The carbon, nitrogen, and sulphur are therefore in the proportion

to constitute three equivalents of sulphocyanogen. Their union with one equivalent of platinum forms the new radical, which takes up another equivalent of potassium in constructing the above salt.

The name proposed for the new substance is *platino-tersulphocyanide of potassium*, and the formula

$$KPtC_6N_3S_6, \text{ or } KPt\,3\,CyS_2.$$

The theoretical and experimental numbers are subjoined:

		Theory.		Experimental mean.
1 equiv. of	potassium	39	12·52	12·73
1 „	platinum	99	31·73	31·63
6 „	carbon	36	11·53	11·72
3 „	nitrogen	42	13·46	13·58
6 „	sulphur	96	30·76	30·83
		312	100·00	

There has been, therefore, in the reaction a simple substitution of 3 equivs. of sulphocyanogen for 3 equivs. of chlorine in the chloroplatinate of potassium employed Expressed in equation;

$$K, PtCl_3 + 3\,KCyS_2 = KPt\,3\,CyS_2 + 3\,KCl.$$

An interesting method of controlling this formula presented itself in estimating the quantity of sulphocyanogen in the compound, thus comprising in one analysis the whole of the carbon, nitrogen, and sulphur present. A solution of the salt was precipitated by sulphide of ammonium, and heated on the water-bath until all trace of free ammonia was lost. After adding acetic acid, the bisulphide of platinum was filtered off, and the clear liquid treated with nitrate of silver. The formation of acetate of silver was prevented by addition of a few drops of nitric acid.

0·7150 grms. of substance gave 1·1275 grms. of sulphocyanide of silver, equiv. to 0·3999 grms. of sulphocyanogen. Calculated for 100 parts.

	Required.	Found.
3 equivs. of sulphocyanogen	55·76	55 90

We may therefore safely infer the correctness of the following equation:

$$K, PtC_6N_3S_6 + 2\,NH_4S = PtS_2 + KCyS_2 + 2(NH_4CyS_2).$$

Subplatino-tersulphocyanide of mercury appears immediately as a copious curdy precipitate on adding nitrate of suboxide of mercury to a solution of the new potassium salt. It is of a deep orange colour, which changes to a pale primrose-yellow on raising the liquid to ebullition. After washing, it was gathered on a filter, pressed with paper, and dried *in vacuo* over sulphuric acid. Freed from water it will bear a considerable temperature without change. Heated in the air-bath to between 140° and 150° C. it suddenly swells up into a singular metallic and arborescent looking substance, showing some resemblance to coarse tea.* At the same time there is a rush of gas which spontaneously kindles.

No further change is observed up to 250°, but below redness, mercurial fumes and cyanogen gas are liberated; and finally, if exposed in an open crucible, the mass fires like tinder, leaving a residue of platinum.

I.	0·5150 grm.	of substance	gave	0·1076 grm.	of platinum.
II.	1·0010 „	„	„	0·2120 „	platinum.
III.	0·9734 „	„	„	0·2052 „	platinum.
IV.	0·9024 „	„	„	0·2534 „	carbonic acid.

which, expressed in 100 parts, give:

	I.	II.	III.	IV.
Platinum	20·87	21·19	21·08	—
Carbon	—	—	—	7·68

agreeing with the formula:

$$Hg_2\,Pt\,3(Cy\,S_2).$$

		Theory.		Experimental mean.
2 equivs.	of mercury	200	42·28	—
1 „	platinum	99	20·95	21·04
6 „	carbon	36	7·61	7·68
3 „	nitrogen	42	8·87	—
6 „	sulphur	96	20·29	—
		473	100·00	

In common with all the examined salts of this series, subplatinotersulphocyanide of mercury yields by dry distillation in a retort, the

* I have not been able sufficiently to examine this compound or arrive at any certain formula. I will only mention that 0·7092 grm. gave by ignition 0·1662 grm. of platinum, which is equivalent to 23·49 per cent.

beak of which is placed under water, much bisulphide of carbon. This circumstance, together with the fact verified by experiment, that nitrogen also is a product, explains the brisk evolution of gas, and ready inflammation of the substance noticed above. The nitrogen gas was identified by conducting the reaction in a sealed tube, and subsequently collecting the gas over water.

Platino-tersulphocyanide of Iron.—When a slightly acid solution of sulphate of iron is added to a concentrated solution of platino-tersulphocyanide of potassium, a black crystalline substance falls, which is insoluble in water, and also in alcohol.

Under the microscope, these grains appear as shining six-sided figures with rounded edges. They are not affected by dilute sulphuric, hydrochloric, or nitric acid, but concentrated nitric acid dissolves them with formation of sulphuric acid. A cold solution of potassa converts them into sesquioxide of iron, and a yellow liquid containing platinum and sulphocyanogen.

To estimate the platinum in this salt, a weighed portion was dissolved in *aqua regia*, and after dilution with water, hydrosulphuric acid was passed in excess, and the precipitate ignited. The filtrate treated with ammonia gave the iron as sesquioxide. The other analyses were made in the usual manner, portions from different preparations being employed.

I.	0·9966 grms.	of substance	gave	0·1334 grms.	of	sesquioxide of iron.
I.	„	„	„	0·3317	„	platinum.
II.	1·0288	„	„	0·1426	„	sesquioxide of iron.
II.	„	„	„	0·3412	„	platinum.
III.	1·0100	„	„	0·1448	„	sesquioxide of iron.
I.	0·9938	„	„	0·4321	„	carbonic acid.
II.	1·0513	„	„	0·4475	„	carbonic acid.
I.	1·0044	„	„	2·1888	„	chloroplatinate of ammonium.
II.	0·5956	„	„	1·3360	„	chloroplatinate of ammonium.
I.	1·07172	„	„	1·6775	„	sulphate of baryta.

The percentage composition is:

	I.	II.	III.
Iron	9·35	9·51	8·99
Platinum	33·29	33·16	—
Carbon	11·85	11·60	—
Nitrogen	13·50	13·96	—
Sulphur	32·08	—	—

The formula is:

$$FePt\,3CyS_2.$$

The theoretical and experimental numbers are:

		Theory.		Experimetal Mean.
1 equiv. of iron		28	9·30	9·28
1 „	platinum	99	32·90	33 23
6 „	carbon	36	11·96	11·73
3 „	nitrogen	42	13.95	13·73
6 „	sulphur	96	31·89	32·08
		301	100·00	

A substance exactly similar in appearance and general character is produced by substituting the salts of the sesquioxide of iron. It falls, however, only on boiling the mixed solutions. A qualitative examination is all that I have been able to bestow upon this compound.

Platino-tersulphocyanide of Silver is prepared by decomposing a solution of the potassium salt by nitrate of silver. It is a heavy curdy substance, of a deep orange colour, which shrinks and agglutinates into a tenacious mass when boiled in water, but again hardens on cooling. A gentle heat causes the dry salt to swell much, igniting with a blue flame if air be present. It is fusible by the blow-pipe into a metallic bead of platinum and silver, by which behaviour it may be readily distinguished from the mercury salt. When recently precipitated it is soluble in cold ammonia, but decomposition ensues at a higher temperature. Nitric acid also acts energetically upon it with disengagement of binoxide of nitrogen; a yellow substance is thrown down; and sulphuric acid is formed during the reaction.

The behaviour of hot caustic potassa towards the silver salt presented a convenient method of estimating the proportional quantities of the platinum and silver contained. By this treatment, 1 equiv. of platino-tersulphocyanide of silver is resolved into 3 equivs. of sulphocyanide of potassium, with precipitation of binoxide of platinum and oxide of silver in the form of a black heavy powder.

$$Ag, Pt\,3(CyS_2) + 3\,KO = 3\,(K, CyS_2) + PtO_2 + AgO.$$

0·6513 grm. of substance gave by igniting the oxides:
0·3538 „ platinum and silver.
0·9038 „ substance gave by ignition in oxygen and air:
0·3061 „ of carbonic acid.

This accords with the above formula for the silver-salt, thus:

		Theory.		Found.
1 equiv. of silver	108	54·33		54·32
1 „ platinum	99			
6 „ carbon	36	9·44		9·10
3 „ nitrogen	42	11·12		
6 „ sulphur	96	25·11		—
	381	100·00		

Here it may be mentioned that the platino-tersulphocyanides, in many respects, bear a strong resemblance to the sulphocyanides. As an example, it may be noticed that both their silver salts form double crystallizable compounds with sulphocyanide of potassium. The parallellism of these two substances is further carried out in their immediate decomposition by dilution with water. In the case of the double sulphocyanide of silver and potassium, a simple separation of the two salts takes place, every trace of silver being thrown down as sulphocyanide. In the double platinum compounds, the reaction consists in a transfer of the potassium to the platinum acid, and precipitation of the silver as sulphocyanide. This last substance (the product of the latter experiment), was identified by analysis, as well as by a careful examination of its properties.* The clear red liquid filtered from the precipitate consisted of a solution of platino-tersulphocyanide of potassium. Expressed by an equation, it stands thus:

$$Ag\ Pt\ 3\ (CyS_2) + KCyS_2 = AgCyS_2 + KPt\ 3\ (CyS_2).$$

Platino-tersulphocyanide of silver is insoluble in an excess of platino-tersulphocyanide of potassium.

Platino-tersulphocyanide of Lead.—This is a remarkably beautiful substance, thrown down in the form of innumerable golden plates, on uniting the concentrated solutions of acetate of lead and platino-tersulphocyanide of potassium. The crystals, which are minute, but

* I. 0·8594 grm. of precipitate, burnt in oxygen and air, gave:
0·2164 „ carbonic acid, or 6·87 per cent of carbon.
II. 0·8548 „ precipitate, burnt in oxygen, &c.. gave:
0·2196 „ carbonic acid, or 6·99 per cent of carbon.

Sulphocyanide of silver requires:

	Calculated.	Experimental mean.
Carbon	7·23	6·94

very regular hexagons, are soluble in alcohol, but less so in cold water, with which they should be well washed on the filter for purification, as recrystallization from a hot solution does not offer a good method, from the speedy deposition of sulphate of lead and disengagement of hydrosulphocyanic acid: an explanation of this decomposition will be offered when we treat of the salts of the next series. The general properties of platino-tersulphocyanide of lead are such as might have been anticipated from the examination of the iron and silver compounds, and leave no doubt of its composition. Attempts were made to obtain analytical numbers, but from the difficulty of procuring the substance chemically pure, they are not sufficiently accurate for insertion.

A subsalt of a brilliant red colour, insoluble in water and in alcohol, is precipitated on substituting the subacetate of lead for the neutral acetate. Its ready solubility in dilute nitric or acetic acid presented the most ready method of estimating the lead in combination, by precipitation as sulphate.

0·5000 grm. of substance gave 0·3100 grm. of sulphate of lead, equivalent to 42·36 parts of lead in 100.

If reliance may be placed upon this single analysis, it satisfactorily points to the basic sulphocyanide of lead as its analogue. The formula for the new compound thus would be:

$$Pb, Pt\,3(CyS_2) + PbO$$

which requires for:

	Theory.	Experiment.
2 equivalents of lead	43·36	43·46

A substance, similar in properties, but much paler in colour, may be procured by the addition of ammonia (not in excess) to the solution of platino-tersulphocyanide of lead.

Hydroplatino-tersulphocyanic acid is most conveniently procured by precipitating a warm concentrated solution of platino-tersulphocyanide of lead by sulphuric acid. The filtrate, which is of a fine red colour, contains the new acid, which is capable of forming all the salts above described, and deports itself in the usual manner of a true acid. From its deep hue, it can be scarcely proved to redden litmus paper, but it presents a decided sour, and then very rough taste to the tongue. It freely displaces carbonic acid from the alkalies, and dissolves metallic zinc with liberation of hydrogen and production of a bright yellow insoluble compound hitherto unexamined. When concentrated on the water-bath, decomposition speedily com-

mences; and on approaching dryness, a brown amorphous mass, very rich in platinum, remains in the dish. By gentle distillation, an acid liquid passes over in considerable quantity, accompanied with the odour of hydrocyanic acid. The distillate furnished with nitrate of silver a copious white precipitate, which on examination proved to be a mixture of cyanide and sulphocyanide of silver. The aqueous and alcoholic solutions of this acid undergo exactly similar reactions at ordinary temperatures, and for this reason I have hitherto failed in procuring the acid in the solid state. By rapid evaporation in the air-pump over sulphuric acid, a confused semi-crystalline mass was obtained; but this gave very little hope of furnishing numbers likely to prove the exact constitution of the acid in its solid condition.

Platino-tersulphocyanide of Barium is a deep red substance, crystallizing in long flattened prisms, or in broad laminæ, often of considerable size. Obtained by dissolving three parts of dry platino-tersulphocyanide of potassium in the solution of one part of chloride of barium in water, or, as an excess of the latter is desirable, it may be in the proportion of nine to four. After evaporation at a gentle heat, the mass may be extracted with hot alcohol, which dissolves nothing but the new salt. It does not appear to be so stable as the potassium-compound.

Platino-tersulphocyanide of Ammonium.—The preparation of this salt by direct union of the acid and base is difficult; that by double decomposition, however, is very convenient. One part of dry sulphate of ammonia may be boiled for a few minutes in a moderately strong solution of 3·5 parts of platino-tersulphocyanide of potassium. The new salt, on cooling, may be separated from the sulphate of potassa and sulphate of ammonia, the last of which is purposely in excess, by alcohol. Another solution in hot water is requisite to obtain it pure, from which the new substance is produced in beautiful crimson hexagonal plates, in figure much resembling the potassium-salt. It is quite stable at ordinary temperatures, but the odour of sulphocyanic acid is readily perceived on boiling the aqueous solution. It gives all the reactions of the potassium-salt.

0·5121 grm.	of substance,	dried *in vacuo*, gave	0·1750 grm.	of	platinum.
0·8615 „	„	burnt in oxygen and air	0·3838 „		carbonic acid.
„	„	burnt in oxygen	0·1212 „		water.

clearly indicating the formula:

$$NH_4, Pt\,3CyS_2.$$

The theoretical and experimental numbers are:

		Theory.		Experiment.
1 equiv. of	platinum	99	34·02	34·17
6 „	carbon	36	12·37	12·14
4 „	hydrogen	4	1·38	1·56
4 „	nitrogen	56	19·24	—
6 „	sulphur	96	32·99	—
		291	100·00	

Platino-tersulphocyanide of Sodium is best procured by precipitating the lead-salt with sulphate of soda. It readily crystallizes in broad garnet-coloured tables, which are soluble in alcohol and in water.

Platino-tersulphocyanide of Copper is precipitated by mixing solutions of sulphate of copper and platino-tersulphocyanide of potassium. It first appears of a brickdust-red colour, which speedily changes at the boiling-heat of the liquid to a black insoluble powder. It gives a fine green solution with ammonia, but the addition of hydrochloric acid reproduces the copper-salt of a dark brown tint.

General remarks upon the foregoing compounds are perhaps better deferred until something has been said with reference to the members of another series which have arisen from the search after analogous compounds to be obtained from protochloride of platinum. I proceed, therefore, to the consideration of:

Platino-bisulphocyanide of Potassium.—Sulphocyanide of potassium dissolves protochloride of platinum with the production of great heat. A red liquid is formed, which by gentle evaporation yields crude crystals of a substance showing in a less marked degree the characteristics of the former group. As in the last case, the best method for procuring it consists in acting upon the double-salt of protochloride of platinum and chloride of potassium (chloroplatinite of potassium*) with sulphocyanide of potassium. They may be taken in equal parts, provided the latter contains no carbonate of potassa or other impurity. It is only necessary that it should be in excess. As the new salt is exceedingly soluble, and crystals are not well obtained by evaporation, the sulphocyanide should be used as a concentrated solution, and not too much of the platinum-salt added at a time, so as to keep the temperature within moderate limits. A

* This is best obtained by neutralizing the hydrochloric solution of protochloride of platinum with carbonate of potassa.

mass of small needles is deposited on cooling, which should be purified from chloride of potassium by strong alcohol, from which again the salt is best recovered by spontaneous evaporation. After pressing between paper, to remove excess of sulphocyanide of potassium, the salt may be once more obtained by gentle evaporation from an aqueous solution.

The crystals appear in stellar groups, and under the microscope show tapering six-sided prisms of a fine red colour, although not so intense as is observable in the potassium-salt of the prior series. At 60° F. they readily dissolve in 2½ parts of water, but their solubility increases at a higher temperature, and in warm alcohol they are soluble to any extent. They are not deliquescent, neither are they, when perfectly dry, apparently affected by a temperature of 100° C.; nevertheless, for analysis, it was preferred to dry them over sulphuric acid in the usual manner.

Nothing worthy of remark is to be observed with reference to the method of obtaining the numerical details here appended.

0·0132 grm. of substance gave, by igniting the precipitate from sulphide of ammonium :
0·3920 „ platinum. The filtrate, evaporated with sulphuric acid, gave :
0·3455 „ sulphate of potash.
1·0055 „ substance, ignited in air and oxygen, gave :
0·3446 „ carbonic acid.
0·7060 „ substance, ignited with soda-lime, gave :
1·2000 „ chloroplatinate of ammonium.
0·5140 „ substance, digested with chlorate of potash and hydrochloric acid, gave :
0·9540 „ sulphate of baryta.

The numbers, for 100 parts, give results which agree most nearly with the formula :

$$KPtC_4N_2S_4 \text{ or } KPt\,2\,(CyS_2).$$

		Theory.		Experiment.
1 equiv. of potassium	39	15·38	15·27
1 „ platinum	99	38·98	38·78
4 „ carbon	24	9·44	9·34
2 „ nitrogen	28	11·02	10·66
4 „ sulphur	64	25·18	25·44
	254	100·00	

The constitution of this salt is therefore quite in accordance with what might be expected from the modification in its construction, and since 2 equivs. of sulphocyanogen are found to replace 2 equivs. of chlorine, the circumstance may be employed as a distinction in its name. For the compound last-described, I propose the designation *platino-bisulphocyanide of potassium*, and for its corresponding acid, *hydroplatino-bisulphocyanic acid*, which, although not euphonious, has the advantage of expressing the arrangement of its elements.

The solution of the pure salt is orange-red; a port wine colour denotes impurity. It copiously precipitates silver and copper-salts, the former of a pale yellow, the latter of a purple-black. No visible change is produced on the nitrate of the suboxide of mercury, except in giving a red tinge to the liquid; and no characteristic precipitates are formed with nitrate of lead or protosulphate of iron, which behaviour marks it off from the platino-tersulphocyanide of potassium, and furnishes some good distinguishing tests. It forms a yellow heavy compound with subacetate of lead, which is readily soluble in acetic and other acids.

Platino-bisulphocyanide of Silver was examined as a control to the formula of the potassium-salt. It is a curdy substance, not unlike sulphocyanide of silver, partially soluble in ammonia, with decomposition. It is soluble in sulphocyanide of potassium, which solution appears to undergo the same change on dilution with water as is observable in the corresponding silver-salt of the previous series.

I. 0·7114 grm. of substance, dried *in vacuo* and fused with carbonate of soda, gave:
0·4552 „ reduced platinum and silver.

II. 0·9518 „ substance, ignited in air and oxygen gas, gave:
0·2324 „ carbonic acid.

III. 1·0137 „ substance, ignited in air and oxygen gas, gave:
0·2595 „ carbonic acid.

IV. 0·6106 „ substance, ignited with soda-lime, gave:
0·8316 „ chloroplatinate of ammonium.

V. 0·4454 „ substance gave, by ignition with chlorate of potash:
0·6084 „ sulphate of baryta.

VI. 0·4494 „ substance gave, by ignition with chlorate of potash
0·6360 „ sulphate of baryta.

Expressed in percentage composition :

	I.	II.	III.	IV.	V.	VI.
Silver } Platinum }	63·98	—	—	—	—	—
Carbon	—	6·89	6·98	—	—	—
Nitrogen	—	—	—	8·53	—	—
Sulphur	—	—	—	—	19·38	19·41

These indicate the formula :

$$Ag\,Pt\,2(CyS_2),$$

as may be seen by comparing the results found, with the theoretical requirements.

		Theory.		Experimental mean.
1 equiv. of	silver	108 }	64·08	63·98
1 „	platinum	99 }		
4 „	carbon	24	7·45	6·94
2 „	nitrogen	28	8·66	8·53
4 „	sulphur	64	19·81	19·40
		323	100·00	

It is scarcely necessary to mention that the salts of both acids form powerful detonating mixtures with chlorate of potassa. The platino-tersulphocyanide of silver in particular inflames with the slightest friction in a mortar, accompanied with a bright flame and loud report. Care is therefore necessary in preparing a mixture for analysis by a large dilution with carbonate of soda.

Hydroplatino-bisulphocyanic acid.—This is best procured by a cautious decomposition of the baryta salt with dilute sulphuric acid. The aqueous solution is speedily decomposed by evaporation, even *in vacuo,* during which process there is an oxidation of the sulphur at the expense of the water. A red or yellow insoluble deposit, rich in platinum and hydrosulphocyanic acid, are the principal bodies formed, the former of which will be noticed in treating of the action of oxidizing agents.

This tendency to absorb oxygen has been slightly touched upon whilst remarking the almost spontaneous decomposition of platino-tersulphocyanide of lead into sulphate of lead and other products. Some knowledge has been also gained whilst searching for an explanation of the frequent escape of carbonic acid attending the

solution of chloroplatinate of potassium in sulphocyanide of potassium.

This effervescence has been traced to the carbonate of potassa, more or less present in the last salt, even when crystallized from alcohol. It was also found that solutions of platino-tersulphocyanide of potassium, assisted by gentle heat, react in a similar manner upon the carbonate with a partial decolorization of the liquid. A red salt crystallizes out, which in no way differs from platino-bisulphocyanide of potassium, whilst the presence of both sulphate and sulphocyanide of potassium is recognized in the filtrate. The first action seems to consist in the partial abstraction of sulphocyanogen from the platino-tersulphocyanide, reducing it to that of the second series. Part of this sulphocyanogen combines with part of the potassium. The sulphur in another equivalent is acted upon by the liberated oxygen, forming sulphate of potassa, whilst the cyanogen is left to combine with the remaining potassium. The carbonic acid escapes as such. This rather complex action may be expressed in an equation which satisfies all the requirements:

$$6\,(K,\ Pt\ 3Cy\ S_2) + 8\,(KCO_3) = 6\,(K,\ Pt\ 2Cy\ S_2) + 2\,(KSO_4) + 5\,(KCy\ S_2) + KCy + 8\,CO_2.$$

A slight modification also represents the change observed in the lead-salt by ebullition with water. The sulphuric acid formed by secondary action isolates the platinum acid:

$$6\,(Pb,\ Pt\ 3Cy\ S_2) + 8\,HO = 6\,(Pb,\ Pt\ 2Cy\ S_2) + 2\,(HSO_4) + 5\,(HCyS_2) + HCy.$$

Long-continued boiling of the aqueous solution of platino-tersulphocyanide of potassium furnishes also the same result.

Action of Ammonia upon the platino-sulphocyanides.—The behaviour of this alkali towards these compounds is interesting, and differs materially from that shewn by bases in general or the fixed alkalies. If carbonate of ammonia be added to a cold saturated solution of platino-tersulphocyanide of potassium, the liquid, after the lapse of a few minutes, fades in colour to a pale yellow; an effervescence sets in; and after two or three hours, a considerable quantity of yellow needles radiate in all directions. The same effect is more expeditiously obtained by using caustic ammonia; but in this case it should not be in a state of concentration, as an insoluble yellow substance generally contaminates the product, and much reduces its quantity. These crystals thrown on a filter, may be well washed in cold water, in which they are but little soluble, and dried without

heat. If required of great purity, they may be again dissolved in warm alcohol, which takes up more of the substance than water. The crystals obtained by this second operation, however, are never so large, but are of a finer colour. The microscope shews them to be long rhombic prisms. Heated in a dry test-tube, they are resolved into free ammonia, hydrocyanic acid, and with access of air, sulphurous acid and metallic platinum. No trace of bisulphide of carbon could be recognized under this treatment, which is a departure from the behaviour of the platino-sulphocyanides in general, and indicates a separation from the group.

0·4885 grm. of salt dried *in vacuo* gave on ignition:
0·2772 „ platinum.
0·8092 „ salt ignited with oxygen and air gave:
0·1986 „ carbonic acid and
0·1320 „ water.
0·5137 „ salt from another sample gave with soda-lime:
1·3033 „ chloro-platinate of ammonium.
0·4578 „ salt ignited with chlorate of potassa:
0·6192 „ sulphate of baryta.

The formula deduced from the percentage composition is:

$$PtC_2H_3N_2S_2,$$

which requires:

		Theory.		Experiment.
1 equiv. of platinum	99	56·89		56·74
2 „ carbon	12	6·89		6·69
3 „ hydrogen	3	1·74		1·81
2 „ nitrogen	28	16·09		15·89
2 „ sulphur	32	18·39		18·55
	174	100·00		

This substance shows therefore a departure from the general series, and indicates a splitting up into compounds of a different type. An examination of the filtrate, after careful addition of hydrochloric acid, plainly proved that the decomposition so often noticed, here again takes place. It was found to contain sulphate of potassa, sulphocyanide of potassium and ammonium, and cyanide of ammonium. The change in the molecular arrangement is expressed thus:

$$6\,(K, Pt\,3\,Cy\,S_2) + 8\,NH_4O = 6\,(Pt\,C_2H_3N_2S_2) + 2\,(KSO_4) + 4\,(KCyS_2) + 2\,(NH_4\,Cy\,S_2) + 5\,(HCy\,S_2) + HCy.$$

The same substance is more readily formed also, by substituting platino-bisulphocyanide of potassium for platino-tersulphocyanide. As the filtrate in this case does not contain a sulphate, the action is very simple:

$$KPt\,2\,Cy\,S_2 + NH_4\,O = PtC_2\,H_3\,N_2\,S_2 + KCyS_2 + HO.$$

A preparation was made after the latter method and ignited, when it was found that,

0·4100 grm. of salt gave 0·1986 grm. of platinum.

Theory requires 56·89. Experiment gave 56·68 per cent.

As the probability was against the above formula truly expressing the constitution of the substance, some light was anticipated by a regrouping of its elementary particles. An intelligible form presented itself on considering the hydrogen and part of the nitrogen as ammonia, which its behaviour at a high temperature appeared to justify, and uniting the carbon, sulphur, and the rest of the nitrogen as sulphocyanogen. Taking sulphocyanide of ammonium as the type, and substituting an equivalent of platinum for one equivalent of hydrogen, we then have the ***sulphocyanide of platosammonium*** (Reiset's first platinum base).

$$N\left\{\begin{matrix}H\\H\\H\\H\end{matrix}\right. Cy\,S_2 \qquad \text{by substitution} \qquad N\left\{\begin{matrix}Pt\\H\\H\\H\end{matrix}\right. Cy\,S_2$$

A ready proof of this supposition presented itself in the direct comparison of the two salts. The preparation of the latter by double decomposition is not difficult. One part of fused sulphocyanide of potassium may be dissolved in water, and 1·6 parts of chloride of platosammonium added. After raising the mixture nearly to the boiling point, an equal bulk of hot alcohol is shaken with the liquid to increase the solubility of the new substance, and the whole is passed, whilst hot, through a filter paper. On cooling, straw-coloured needles are deposited, which exhibit all the properties of the former compound, the identity with which was still further shown by a quantitative analysis.

0·6120 grm. by ignition gave 0·3470 grm. of platinum, representing the formula:

$$PtH_3NCyS_2.$$

The composition for 100 parts requires by theory, 56·89 of platinum; the quantity found was 56·69.

Sulphocyanide of platosammonium is indifferent to the action of dilute sulphuric or hydrochloric acid. The aqueous solution does not affect salts of copper, lead, or mercury, but precipitates nitrate of sulphate of silver as a bulky and pale yellow compound, which is rich in platinum. This precipitate requires more study than has as yet been bestowed upon it. The aqueous solution by long boiling liberates ammonia, and deposits the yellow insoluble substance above alluded to, the composition of which is yet uncertain.* Caustic potassa appears to effect the same change. A temperature between 100° and 110° C. causes the salt to fuse into a clear garnet-coloured syrup, which hardens on cooling, and does not appear to be further affected by a rise to 180° C.

Before dismissing this portion of the subject, there appears to be yet another point of view from which the salt might be regarded. Although no doubt was entertained of the correctness of the last formula, some interest seemed to be attached to the circumstance of its polymerism with another body not hitherto prepared. I have recently had occasion to show that cyanogen gas, acting on oxide of diplatosammonium, produces the platinocyanide of that base, the formula of which is double that assigned by Reiset to the decomposition. The true cyanide of platosammonium, further, may be obtained from the corresponding chloride, by acting with cyanide of potassium. Just in the same manner we might expect a parallelism between platino-bisulphocyanide of diplatosammonium and sulphocyanide of platosammonium. This may be more readily intelligible thus:

$$\underbrace{2(PtH_3N, Cy)}_{\text{Cyanide of plato-sammonium.}} = \underbrace{PtH_6N_2, PtCy_2}_{\text{Platinocyanide of diplatosammonium.}} \text{ and } \underbrace{2PtH_3N, CyS_2}_{\text{Sulphocyanide of platosammonium.}} = \underbrace{PtH_6N_2, Pt2CyS_2}_{\text{Platino-bisulphocyanide of diplatosammonium.}}$$

Platino-bisulphocyanide of diplatosammonium falls as a voluminous flesh-coloured precipitate, on decomposing the chloride of the base by a soluble platino-bisulphocyanide. It is quite insoluble in water, and also in alcohol. Dilute hydrochloric acid dissolves it rather freely. When heated on platinum foil, it liberates ammoniacal gas, fuses into a black bubbling mass, and then burns tinder-like to a bright platinum sponge.

0·8576 grm. of substance ignited,			gave 0·4896 grm.	of	platinum.
„	„	ignited in oxygen	„ 0·2090	„	carbonic acid.
„	„	ignited in oxygen	„ 0·1460	„	water.
0·2656	„	ignited with chlorate of potassa and carbonate of soda	„ 0·1512	„	platinum.
			„ 0·3617	„	sulphate of baryta.

* A well-washed sample gave on ignition as much as 92·27 per cent of platinum. It contains sulphur and the elements of ammonia.

leading to the formula :

$$PtH_6N_2,\ Pt\ 2(CyS_2).$$

The theoretical and experimental numbers are appended.

		Theory.		Mean found.
2 equivs. of platinum		198	56·90	56·94
4 „	carbon	24	6·90	6·65
6 „	hydrogen	6	1·72	1·89
4 „	nitrogen	56	16·09	—
4 „	sulphur	64	18·39	18·62
		348	100·00	

On the action of Chlorine Gas and Nitric Acid upon the Platino-sulphocyanides.—An examination in this direction seemed to be desirable, from the belief that the above decomposition did not show the full extent of oxidation, to which the salts of either series might be carried. When commenting upon the acids, it was mentioned that their aqueous solutions were resolved by heat into a red or brown amorphous substance, hydrosulphocyanic and sulphuric acids. The same brown compound is formed by pouring warm concentrated nitric acid on the powdered potassium salts. Experiment also proved that if a warm and rather concentrated solution of platino-tersulphocyanide of potassium be subjected to a stream of chlorine, the temperature rises considerably during the absorption of the gas. By decomposition of water, the chlorine passes into hydrochloric acid, and the liberated oxygen converts the greater part of the sulphur into sulphuric acid. The first of these acids may be removed by evaporation on the water-bath, and the latter, after careful neutralization with carbonate of soda, by a thorough washing with hot water, which at the same time carries off the whole of the potassa as bisulphate.

During evaporation, the odour of hydrocyanic acid is very perceptible. The new substance on the filter appears of all shades of colour, from a bright red to a dirty brown. It may be dried at a gentle heat, and then has the form of a light non-crystalline powder, strongly soiling the hands, insoluble in water and in alcohol, but before drying slightly soluble in hydrochloric acid. It is unaffected by a solution of potassa, but ammonia changes its colour to a yellow hue.

When ignited in a close crucible, vapours of bisulphide of carbon and cyanogen gas are disengaged, and the solid residue consists of bisulphide of platinum. The action of concentrated nitric acid is quite similar. Hydrocyanic acid and nitrous fumes are given off, and in general the insoluble residue is produced of a brighter colour.

The following numbers were obtained on its analysis:

0·3700	grm.	of substance ignited .	gave 0·2304	grm.	of platinum.
0·8964	„	burnt in oxygen	„ 0·2800	„	carbonic acid.
„	„	burnt in oxygen	„ 0·0320	„	water.
0·7334	„	burnt with soda-lime	„ 1·1600	„	chloroplatinate of ammonium.
0·5146	„	burnt with chlor. of potassa	„ 0·7048	„	sulphate of baryta.
1·0704	„	a different sample	„ 0·6639	„	platinum.
„	„	burnt with oxygen	„ 0·3426	„	carbonic acid.
„	„	burnt with oxygen	„ 0·0448	„	water.

I regret that I have been unable to prepare this substance in such a state of purity as to place its true composition beyond all doubt. I had anticipated from its mode of formation a substance which bears towards the platino-sulphocyanides, the same relation which the so-called solid sulphocyanogen bears towards the sulphocyanides. If, however, we calculate the water as such, it will give an excess in the experiments of more than 3 parts in the 100 taken; and the discrepancies between the other constituents will be found as great. I am therefore inclined to suppose that the hydrogen is partly accidental, and that as the formula adopted has the recommendation of great simplicity, and satisfies all the conditions observed in the reaction, it will ultimately prove to be correct. I have thought it better, in addition to the theoretical and experimental numbers, to give the ratio in parts of a unit between the component parts, which places their relation in a clearer point of view. The formula of protosulphocyanide of platinum is:

$$PtCyS_2.$$

		Theory.		Found.		Mean.	Ratio.
1 equiv. of	platinum	99	63·05	62·27	62·02	62·14	1·0
1 „	carbon	12	7·64	8·53	8·72	8·62	2·3
1 „	nitrogen	14	8·93	9·92	—	9·92	1·1
2 „	sulphur	32	20·38	18·77	—	18·77	1·9
		157	100·00				
	Hydrogen . . .			0·39	0·15	0·42	0·6
						99·87	

There remains only to show by equation this decomposition by chlorine gas. The reaction is strictly in character with those before noticed.

$$K, Pt\,3\,CyS_2 + 11Cl + 16\,HO = PtCyS_2 + \left.\begin{matrix}K\\H\end{matrix}\right\} 2\,SO_4 + 2\,HSO_4 + 11HCl + 2\,HCy.$$

The platino-sulphocyanides possess characters so distinct from other salts, that there is no likelihood of confounding them with other known compounds. They are all highly coloured, and take all gradations from pale and bright yellow to deep red. This colour appears attendant, in a great measure, upon the quantity of sulphur combined with the platinum, since the intensity is more remarkable in the first than in the latter series, and is nearly lost in the sulphocyanide of platosammonium.

Their ready inflammability, and peculiar odour when gently heated, may also be considered as characteristic. The separation of the two series is well marked by their different action on reagents, which for better illustration has been arranged in the following table, representing the precipitation or non-precipitation of a soluble salt of each series.

Reagents.	Platino-tersulphocyanides.	Platino-bisulphocyanides.
Subsalts of mercury . . .	Orange precipitate . . .	No precipitate, liquid changes colour on heating.
Salts of silver	Red or orange precipitate	Pale yellow precipitate.
Protosalts of iron	Black shining grains . .	No change.
Salts of copper	Brick-red precipitate . .	Purplish-black precipitate.
Subsalts of copper . . .	Rich brown precipitate .	Purplish-black precipitate.
Salts of cobalt	Orange-red precipitate .	No change.
Salts of lead	Soluble golden laminæ .	No change.
Basic salts of lead . . .	Fine red precipitate . .	Pale yellow precipitate.
Persalts of gold	Salmon-coloured precipitate	Salmon precipitate.
Ferrocyanide of potassium .	Prussian blue formed on boiling	A nearly white precipitate on boiling.
Chromic acid	No precipitate	A copious reddish precipitate, with evolution of hydrocyanic acid.
Salts of platosamine . . .	Copious orange precipitate	Fine yellow precipitate.
Salts of diplatosamine . .	Fine vermilion-red precipitate.	Flesh-coloured precipitate.

The ready conversion of the sulphur in these compounds into sulphuric acid, in presence of water, is shown in an interesting manner by their action upon metallic zinc. Aqueous solutions of the potassa salt are resolved into platinum black, hydrosulphocyanic acid, sulphate of potassa, and free sulphuric acid, which, acting upon the zinc, liberates a considerable quantity of hydrogen gas.

A few general remarks upon the constitution of the platino-sulphocyanides may not be considered here misplaced. Viewing them according to Berzelius's explanation of the ferrocyanides, they must

be taken as double compounds of protosulphocyanide and bisulphocyanides of platinum with a metallic sulphocyanide, or hydrosulphocyanic acid;

Platino-cyanides.	Platino-bisulphocyanides.	Platino-tersulphocyanides.
$M\,Cy + Pt\,Cy$	$M\,Cy\,S_2 + Pt\,Cy\,S_2$	$M\,Cy\,S_2 + Pt\,2\,Cy\,S_2$

whilst, on the more generally received idea, they contain two separate radicals of acid character, forming salts upon the hydrochloric acid type. The similarity of action between sulphur, oxygen, chlorine, cyanogen, &c., in combination has been frequently remarked. Instances of substitution of sulphur for chlorine may be seen in the reactions of sulphide of potassium upon hydrochloric ether and Dutch liquid.

Throughout this Paper, I have assumed the existence of chloroplatinous and chloroplatinic acids, from the close similarity they bear towards the platino-sulphocyanides; and I think an argument in favour of their existence may be found in the construction of the latter from the former by simple substitution of sulphocyanogen for chlorine. In the same manner we construct the platino-cyanides, by exchanging chlorine for cyanogen, although at present we want the higher number in the series. This will, doubtless, turn up upon a careful search. We have thus:

Platino-chlorides or chloro-platinides.	Platino-cyanides.	Platino-sulpho-cyanides.
$M, Pt\,Cl_3$	missing	$M, Pt\,3\,Cy\,S_2$
$M, Pt\,Cl_2$	$M, Pt\,Cy_2$	$M, Pt\,2\,Cy\,S_2$

Some interest attaches to the new acids from the large number of sulphur-atoms they contain.

Platino-tersulphocyanide of potassium presents, I believe, the first instance of the union of sulphur with the triple cyanogen group, represented by the cyanurates, in which all the oxygen is replaced by sulphur. The analogy is not, however, strict between them, since it will be seen that in the new compounds only 2 equivs. of hydrogen are replaced by metals. The same objection does not apply with reference to the fulminates.

In conclusion, notice should be taken of a crystalline compound described by Claus, which is prepared by acting upon bisulphocyanide of mercury with sulphocyanide of potassium. From the formula given, which is $K\,Cy\,S_2 + 2\,Hg\,Cy\,S_2$, it is clearly a double compound, and therefore has but little resemblance or connection with the substances above described.

III.—*Analysis of the Ash of Lemon-Juice.*

By Henry M. Witt,

Assistant in the Royal College of Chemistry (the Laboratories of the Metropolitan School of Science.)

The following analysis, having for its object the determination of the mineral constituents in the juice of lemons, was made during the early part of last summer, in the laboratory of the Royal College of Chemistry, under the superintendence of Dr. Hofmann, and at the request of Dr. Bence Jones.

Preparation of the Ash.—The lemons (200 in number) were peeled with a bright steel knife, care being taken in so doing to avoid as much as possible cutting into the juicy endocarp, and thus bringing the acid in contact with the steel knife; the juice was then expressed by a hand-squeezer of wood (without any metallic hinges), and filtered through flannel into a porcelain dish, in which it was evaporated to the condition of a black carbonaceous mass, then transferred, a portion at a time, into a platinum dish, and ignited until perfectly white.

A *qualitative examination* was first made, which indicated the presence of potassa, soda, lime, magnesia, and sesquioxide of iron; of silicic, phosphoric, sulphuric, hydrochloric, and carbonic acids. A separate and very careful examination was made for alumina, but it was not detected; manganese was also separately tested for, but not found.

As regards the plan followed in performing the *quantitative analysis*, it differed in no respect from that generally adopted.

Without entering into details, it may be stated that the part insoluble in hydrochloric acid consisted of silica and carbonaceous matter. In one portion of the hydrochloric solution, the phosphate of iron, the lime, magnesia, and phosphoric acid, were determined; whilst separate portions of the solution were employed for the alkalies and for sulphuric acid; a nitric acid solution being used for the determination of hydrochloric acid; and, lastly, a distinct portion of the ash was reserved for estimating the carbonic acid.

The phosphoric acid was determined as ammonio-magnesian-phosphate in the dilute solution, to which acetate of potassa had been added, after separation of the lime by oxalic acid.

The following are details of the results obtained.

1. Determination of silica.

	Weight of ash employed.	Silica obtained.	Percentage.
I.	59·3835 grns.	0·355 grn.	0·5986
II.	23·6165 „	0·128 „	0·542

2. Determination of carbon.

	Weight of ash employed.	Carbon obtained.	Percentage.
I.	59·3835 grns.	0·0615 grn.	0·1035

3. Determination of phosphate of iron.

	Weight of ash employed.	Phosphate of iron obtained.	Percentage.
I.	24·5077 grns.	0·230 grn.	0·9385
II.	18·276 „	0·219 „	1·198

4. Determination of lime.

	Weight of ash employed.	Carbonate of lime obtained.	Percentage of lime.
I.	24·5077 grns.	3·354 grns.	7·6631
II.	18·276 „	1·353 „	7·4059

5. Determination of magnesia.

	Weight of ash employed.	Pyrophosphate of magnesia obtained.	Percentage of magnesia.
I.	18·276 grns.	1·644 grns.	3 2124
II.	23·6165 „	2·2385 „	3·385

6. Determination of phosphoric acid.

α. In combination with lime:

	Weight of ash employed.	Pyrophosphate of magnesia obtained.	Percentage of phosphoric acid.
I.	18·276 grns.	0·402 grns.	1·4146
II.	16·242 „	0 520 „	2·0582

β. In combination with magnesia:

	Weight of ash employed.	Pyrophosphate of magnesia.	Percentage of phosphoric acid.
I.	18·276 grns.	1·644 grns.	5·7825
II.	23·616 „	2·2385 „	5·7106

7. Determination of the alkalies.

	I.	II.
Weight of ash employed	10·84 grns.	11·948 grns.
Weight of mixed chlorides obtained	7·970 „	9·04 „
Corresponding to per cent of mixed alkalies (KO and NaO)	45·9355	45·9446
Weight of potassium platinum-salt ($KCl, PtCl_2$) obtained	25·077 „	26·700 „

hence:

Percentage of potassa	44·251 „	43·545
„ soda	1·6845 „	2·3996

8. Determination of sulphuric acid.

	Weight of ash employed.	Sulphate of baryta obtained.	Percentage of sulphuric acid.
I.	8·7795 grns.	3·159 grns.	12·354
II.	6·018 „	2·069 „	11·802

9. Determination of carbonic acid.

	Weight of ash employed.	Carbonic acid evolved.	Percentage.
I.	15·517 grns.	3·02 grns.	19·462

10. Determination of chlorine.

	Weight of ash employed.	Chloride of silver obtained.	Percentage.
I.	8·7795 grns.	0·429 grns.	1·2079 grns.
II.	6·018 „	0·295 „	1·2090 „

The following table is a synopsis of the preceding results:

	I.	II.	mean.
Alkalies (KO and NaO)	45·9355	45·9446	45·9400
Potassa . . .	44·251	43·545	43·8984
Soda . . .	1·6845	2·3996	2·1416
Lime . . .	7·6631	7·4059	7·5345
Magnesia . . .	3·2124	3·385	3·2987
Sulphuric acid . .	12·3540	—	12·3540
Chlorine . . .	1·209	1·2079	1·2084
Carbonic acid . .	19·462	—	19·4620
Phosphoric acid .	7·1971	7·7691	7·4829
Phosphate of iron .	0·9385	1·198	1·0682
Silica . . .	0·5986	0·542	0·5700
Carbon . . .	0·1035	—	0·1035
Alumina, Manganese } absent.			
			99·1222

The preceding numbers, after deducting the charcoal, give the following as the percentage composition of the ash:

Potassa	44·34
Soda	2·16
Lime	7·61
Magnesia	3·34
Sulphuric acid . . .	12·47
Carbonic acid . . .	19·66
Chlorine	1·23
Phosphoric acid . . .	7·56
Phosphate of iron . .	1·06
Silica	0·57
	100·00

These constituents may be assumed to be thus arranged:

Carbonate of potassa	57·725
Carbonate of soda	2·265
Sulphate of potassa	9·293
Chloride of sodium	2·026
Sulphate of lime	13·935
(Tribasic) Phosphate of lime . .	3·687
Phosphate of magnesia . . .	9·086
Phosphate of iron	1·060
Silica	0·570
	99·647

In order to ascertain the proportion of ash in the juice, a known weight was carefully incinerated in a platinum dish, with the following results:

	Weight of juice employed.	Ash obtained.	Percentage.
I.	587·96 grns.	3·11 grns.	0·52
II.	1020·695 „	2·055 „	0·20
		Mean	0·36

Hence by calculation, the following was obtained as the proportion of the several *inorganic constituents of the juice:*

	Inorganic constituents of 1000 grains of the juice.	Inorganic constituents of an ounce Troy (480 grns.) of the juice.
Potassa . .	1·597 grns.	0·767 grns.
Soda . .	0·077 „	0·038 „
Lime . .	0·274 „	0·131 „
Magnesia . .	0·120 „	0·058 „
Sulphuric acid .	0·448 „	9·215 „
Chlorine . .	0·045 „	0·022 „
Carbonic acid .	0·707 „	0·339 „
Phosphoric acid .	0·273 „	0·130 „
Phosphate of iron	0·038 „	0·018 „
Silica . .	0·021 „	0·010 „
Total	3·600	1·728

On reviewing the above-mentioned results, it was felt that the objection might by raised, that either the whole or at least a portion

of the iron found, might have been derived from the knife employed in cutting the lemons (notwithstanding the precautions taken to avoid contamination from this source); consequently, to remove all doubt on this rather important point, a fresh portion of juice was incinerated, the lemons whence it was obtained having been cut with a silver knife, and every possible care taken to avoid the extraneous introduction of iron. In the ash thus obtained the determination of the ferruginous phosphate was repeated with the following result:

Weight of ash employed.	Phosphate of iron obtained.	Percentage.
8·225 grns.	0·12 grn.	1·458

which, on comparison with the preceding, lead to the conclusion that none of the iron had been derived from the knife, since this last determination indicates a still larger proportion of the phosphate than either of the former determinations.

IV.—*Note on Platinum accompanying Silver in solution in Nitric Acid.*

By Henry How,

(assistant to professor anderson.)

Having occasion recently to reduce some silver for use in the laboratory of Professor Anderson, in Glasgow, from the collection of precipitates and filters preserved for the purpose, I observed a phenomenon, which, so far as I am aware, has not been noticed, and which I make known to the Society in the hope of some of its members being able to afford further information on the subject. It is a well-known fact that platinum in alloy with silver does dissolve in nitric acid, but I have not been able to meet with an account in any analytical work of what I observed, as to its behaviour when so dissolved.

Among the precipitates and filters alluded to, although it was intended that none but salts of silver should be present, it appears from the facts I am about to state, some containing platinum mixed with silver, the results of certain investigations of Professor Anderson, had been introduced. I set about obtaining the silver in the usual way, by drying up and burning the mass of residues and paper in an iron dish, and subsequently fusing the charred mass with

carbonate of soda, and some borax to dissolve any iron which might have scaled off from the said dish. A button of silver was obtained, which I proceeded to treat with nitric acid. I was surprised to find a blackish-brown powder remain undissolved, while the whole of the silver, and it alone, as I thought, went up in the acid. On examining the powder, I found it to contain silver, but in what state of combination I could not determine; at the time I imagined it to be a boride, but I am now inclined to think it must have contained platinum. I regret, from what I observed afterwards, I did not submit it to a more rigorous analysis.

The acid solution of the supposed pure silver was evaporated to complete dryness, and gently heated to expel the excess of nitric acid; the residue was then dissolved in a comparatively small quantity of water, as a strong solution was desired; a little yellowish-brown powder remaining undissolved, the fluid was filtered. On diluting a small portion of this liquid with distilled water, I was surprised at seeing a white precipitate fall, and was disposed to imagine that by some inadvertence, some salts of bismuth or antimony had been thrown among the silver residues; however, neither of these metals could be detected. The whole fluid was then diluted and allowed to stand a day; a precipitate formed, from which the solution was poured off and again allowed to stand. It had rather a turbid appearance, and I observed a sediment gradually form, in the shape of pale yellow amorphous flocks, which went on increasing; after about a week, this was collected on a filter, washed with water, and examined. The sediment was found to dissolve completely in ammonia, and for the most part in acetic and in nitric acid. In these acid solutions, hydrochloric acid gave a large precipitate, which proved to be chloride of silver; and in the fluid separated from this, platinum was found to be present in abundance. Although I did not certainly detect nitric acid, I am disposed to imagine, from the nature of the process by which it was obtained, that this sediment must have been some basic double-salt of silver and platinum with nitric acid, the liquid from which it deposited having an acid reaction. I may mention that, it being found that platinum was present, I precipitated the whole of the silver in the remaining fluid by hydrochloric acid, and reduced it after washing, by iron, and so succeeded in obtaining a pure salt of silver.

I have ventured to offer this note to the Society, as containing a fact, I believe, new and worthy of consideration in cases of analysis where silver and platinum may occur together in an alloy; as, without any intimation of the existence of such a compound as

that which spontaneously deposits from an aqueous solution of nitrate of silver containing platinum, the analyst may be as much surprised as I was to observe its formation, and unable to account for it at once. I also think the brown powder, which I have described as remaining after the solution of the alloy by digestion in ordinary nitric acid, is worthy of attention and further notice.

V.—*Note on the Valuation of Protochloride of Tin.*

By Dr. Penny, Glasgow.

In a paper on the Valuation of Red Prussiate of Potash, published in the "Quarterly Journal of the Chemical Society,"* Mr. Francis Leishing states an objection to the process for estimating the amount of tin in double muriate of tin by bichromate of potash. His words are: "In this instance, the liquid double muriate of tin might contain a very considerable admixture of protochloride of iron, without even changing its external appearance; and this in practice highly obnoxious admixture would, by the sole application of the bichromate of potash test, not only escape detection, but the iron would actually be calculated as tin."

As this statement may lead some to reject the process without trial, or, perhaps, induce some manufacturer of these tin-solutions to infer that protochloride of iron could be added to chloride of tin without risk of detection, it may be as well to show that Mr. Leishing's objection is really without foundation.

It is quite obvious that if acetate of lead be exclusively relied upon as the agent for determining when a sufficient quantity of the bichromate of potash has been added, the process will be vitiated by the presence of iron.

In the description of the process, however,† it is particularly mentioned that the "sulphocyanide test," consisting of a mixture of protosulphate of iron and sulphocyanide of potassium, is much more delicate and satisfactory than acetate of lead. This test completely removes the objection arising from the presence of iron.

Sesquichloride of iron cannot exist in the same solution with protochloride of tin; and accordingly no sesqui-compound of iron can be

* Vol. VI, 31. † Quarterly Journal, IV, 239.

formed during the addition of the bichromate, until the protochloride of tin is wholly converted into bichloride, and then the further addition of bichromate instantly produces sesquichloride of iron, the smallest trace of which is immediately revealed by the sulphocyanide test. In point of fact, instead of protochloride of iron "escaping detection," and being "calculated as tin," as Mr. Francis Leishing affirms, its presence would actually assist the operator in catching the precise moment when the conversion of protochloride of tin into bichloride is perfected. It might indeed be an advantage to add a small quantity of a proto-compound of iron to the tin solution, in place of mixing sulphate of iron with the sulphocyanide of potassium, as directed in the paper referred to.

The addition of protochloride of iron to double muriate of tin would in practice be a truly obnoxious admixture, but its presence could in no way interfere with the bichromate process for the valuation of tin crystals, double muriate of tin, &c., provided the proper test be employed.

It certainly seems almost unnecessary to notice the objection, as every one acquainted with the applications of these tin preparations must be aware that adulteration with iron would very soon manifest itself in the course of the usual operations.

The justness of Mr. Leishing's remark upon the importance of alkalimetric methods of valuation being preceded by qualitative testing of the substance under examination will readily be admitted, and especially as the same observation may be extended to nearly all our ordinary processes of analysis.

VI.—*On the so-called Iodide and Chloride of Nitrogen.*

By J. H. Gladstone, Ph.D. F.R.S.

On the 17th of February, 1851, I communicated to the Chemical Society a paper on the Explosive Compound usually denominated Iodide of Nitrogen, in which I assigned to it the composition NHI_2. The paper was printed in the following "Quarterly Journal." In the "Annalen der Chem. und Pharm." for October, 1852, Bunsen published an investigation of the composition of the same substance, in which he ascribes to it the formulæ $NH_3 + NI_3$, and $NH_3 + 4NI_3$, according to different modes of preparation. At first sight, there would seem

an irreconcilable discordance between the results of his analyses and mine; but on closer examination this disappears, for both the methods by which he prepared the explosive powder differ from that adopted by me. He, forming the substance from iodine and ammonia dissolved in absolute alcohol, and never suffering it to come in contact with water, finds it to be $NH_3 + NI_3$; forming it by precipitating a solution of iodine in *aqua-regia* by aqueous ammonia, and washing it with water, he finds it to be $NH_3 + 4\,NI_3$. I, forming the substance by precipitating an alcoholic solution of iodine by ammonia, and washing with water, found it to be NHI_2, which is equivalent to $NH_3 + 2\,NI_3$ on Bunsen's mode of expression, and is intermediate between his two formulæ. Nevertheless I thought it desirable to repeat my former analysis, and to add some further observations towards the completion of the chemical history of this remarkable substance.

Bunsen does not adopt my method of analysis, but takes advantage of the reaction between hydrochloric acid and the black powder, which is fully explained towards the close of my paper. As, however, my method by sulphurous acid gives very exact results, I had recourse to it again. A portion of the explosive substance prepared and washed as before, and decomposed by a fresh solution of sulphurous acid, was divided into two equal parts, and yielded 0·632 grm. of iodide of silver, 0·620 grm. of sulphate of baryta, and 0·124 grm. of platinum derived from the ammonia-salt. Traces of nitrogen gas were given off during the destruction of the black powder, the amount of which was estimated at 0·04 cub. in. Half of this would be equal to 0·0004 grm. weight of nitrogen, which must be added to the amount found to have been converted into ammonia. The numbers given above indicate:

Nitrogen . . .	0·0182 grm.
Iodine . . .	0·3404 „
Sulphuric acid . .	0·2131 „

which, divided by the atomic weights, give:

Nitrogen . .	130 or 1 equiv.
Iodine . .	268 or 2·06 „
Sulphuric acid .	533 or 4·10 „

This, indicating the proportion of iodine to nitrogen as 2 : 1, agrees perfectly with the result of the analyses recorded in my previous paper.

In another experiment, similarly conducted, there were obtained

0·441 grm. of iodide of silver and 0·281 grm. of ammonio-chloride of platinum. The same amount of nitrogen gas may be reckoned as having been evolved during the action of the sulphurous acid. These numbers indicate:

Nitrogen . . .	0·0142 grm.
Iodine . . .	0·2375 „

which, divided by the atomic weights, give:

Nitrogen . .	101 or 1 equiv.
Iodine . .	187 or 1·85 „

This analysis, though it indicates rather too small a quantity of iodine, does not differ materially from the preceding.

My former view of the composition of the explosive powder prepared by precipitating an alcoholic solution of iodine by ammonia, and washing with water, is therefore confirmed. The question remains, whether the substance is to be considered one atom of ammonia, in which two of the equivalents of hydrogen are replaced by iodine—in fact, iodimide; or whether it is to be viewed, in accordance with Bunsen's formulæ, as ammonia combined with two equivalents of teriodide of nitrogen? Now a body of the composition assigned by the German chemist to his explosive powder, NH_3+NI_3, might be equally well expressed as a compound of my NHI_2 with NH_2I:

$$NH_3+NI_3=N_2H_3I_3=NHI_2+NH_2I,$$

Both NI_3 and NH_2I are alike hypothetical substances; yet it appeared very possible that the action of water on the compound might throw some light upon the subject. It was found that when the black powder formed in the presence of water was washed for a great length of time, the washings still continued alkaline to test-paper. Black powder which had been produced by mixing solutions of iodine and ammonia in alcohol of sp. gr. 814, and had been well washed with the same alcohol, gave, on the addition of water, a solution which was distinctly alkaline and of a slight red tint. This colour was removed by the very least addition of sulphurous acid solution. Precisely the same was observed when the explosive powder was prepared by means of absolute alcohol. A quantitative estimation was made of the washings by water of the substance precipitated in alcohol of sp. gr. 814. Water had been passed through it on a filter for thirty minutes. The slightly red solution was decolorized by a

drop of sulphurous acid; it was divided into two equal parts, from one of which 0·047 grm. of iodide of silver was obtained, and from the other 0·028 grm. of platinum derived from the ammonio-chloride. These numbers indicate:

Nitrogen . . .	0·0040 grm.
Iodine . . .	0·0253 „

which, divided by the atomic weights, give:

Nitrogen . .	28 or 1 equiv.
Iodine . .	20 or 0·71 „

Hence, there must have been free ammonia as well as iodide of ammonium, a result rather favouring the view taken by Bunsen.

The above-mentioned specimen of explosive iodide prepared by means of alcohol, sp. gr. 814, was analysed by sulphurous acid, as in the preceding instances. The amount of nitrogen gas given off was too inconsiderable to be taken account of. The weights of the precipitates obtained were 0·256 grm. of ammonio-chloride of platinum, 0·630 grm. of iodide of silver, and 0·649 grm. of sulphate of baryta, which indicate:

Nitrogen . . .	0·0162 grm.
Iodine . . .	0·3394 „
Sulphuric acid . .	0·2230 „

These quantities, added to those previously found, dissolved in water, are:

Nitrogen . . .	0·0202 grm.
Iodine . . .	0·3647 „
Sulphuric acid . .	0·2230 „

which, when divided by the atomic weights, give:

Nitrogen . .	144 or 1 equiv.
Iodine . .	286 or 1·98 „
Sulphuric acid .	557 or 3·86 „

This result perfectly coincides with the previous analyses. The composition of this specimen of explosive powder was also NHI_2.

The unexpected confirmation of my previous views afforded by this experiment induced me to analyse a sample of the black precipitate

thrown down by mixing solutions of iodine and of ammonia* in absolute alcohol. The experiment was conducted with great care, to prevent the hydration of the alcohol in any possible way during the course of it. The black powder obtained had precisely the same physical appearance as the specimens previously examined. It was decomposed and analysed in the usual manner. The amount of nitrogen gas evolved was 0·06 cub. in., half of which would weigh 0·0006 grm. The weights of the precipitates obtained were 0·253 grm. of ammoniochloride of platinum, 0·539 grm. of iodide of silver, and 0·498 grm. of sulphate of baryta, which indicate:

Nitrogen . . .	0·0166 grm.
Iodine . . .	0·2903 „
Sulphuric acid . .	0·1711 „

These numbers, divided by the atomic weights, gave:

Nitrogen . .	118 or 1 equiv.
Iodine . .	228 or 1·93 „
Sulphuric acid .	428 or 3·63 „

But these proportions approximate those of all my previous analyses. It is easily conceivable that different proportions of hydrogen should be replaced in different specimens, but by what variation of circumstances I obtained the substance NHI_2, instead of that analysed by Bunsen, I know not. I can but record the result of my experiment.

When the black powder is formed in the presence of water, half, or very nearly half the iodine employed is obtained in the solid compound, and the solution becomes colourless, or nearly so, the reaction being:

$$4\,I + 3\,NH_3 = NHI_2 + 2\,NH_4I,$$

but when the iodine and ammonia are brought together in solution in strong alcohol, a far smaller proportion of the black powder is obtained, and the liquid remains deep-red in colour, although the

* Before the ammonia is dissolved in the absolute alcohol, it is necessary that it be dried. The desiccation of this gas is, I believe, usually effected by passing it over pieces or sticks of hydrate of potash; but I adopted another process. It was made to pass through a wash-bottle containing absolute alcohol, into which some pieces of potassium had been thrown. Thus was secured the advantage of the gas bubbling through a liquid, and that liquid a most hygroscopic solution of ethylate of potash perfectly free from water. Of course this process is only applicable for the desiccation of ammonia, in cases where the vapour of alcohol does not interfere.

ammonia be added in large excess. A considerable amount of sulphurous acid solution also is required to effect its decolorization. The addition of water causes a black precipitate, which however being in a very finely-divided condition, is speedily acted upon by the water, and decomposed with evolution of gas—doubtless nitrogen. It is evident, therefore, that although iodide of ammonium is soluble in alcohol, some other compound must be here formed. The ratio between the iodine in solution and that in the precipitate, was thrice determined; as also the ratio between the hydriodic acid and the sulphuric acid formed upon decomposing the red liquid by sulphurous acid. In the first experiment, alcohol of sp. gr. 814 was employed; in the second and third, absolute alcohol was made use of. The results were:

	Exp. I.	Exp. II.	Exp. III.
Iodide of silver from black powder	1·220 grm.	0·898 grm.	0·539 grm.
„ „ „ red solution	3·255 „	3·595 „	4·376 „
Sulph. of baryta „ „	0·950 „	1·061 „	1·543 „

The proportion between the two estimations of iodine in these three experiments is widely different, namely:

	Exp. I.	Exp. II.	Exp. III.
From black powder	1	1	1
From red solution	2·67	4·00	8·12

The ratio between the iodine and the sulphuric acid formed from the red solution, agrees more closely, namely:

	Exp. I.	Exp. II.	Exp. III.
Iodine	1 equiv.	1 equiv.	1 equiv.
Sulphuric acid	0·59 „	0·60 „	0·71 „

The smaller proportion of sulphuric acid would appear to indicate that the iodine exists in the red solution to a considerable extent in the form of iodide of ammonium; but it must be mixed or combined with a larger amount of the element in some other condition.

In the third experiment, the ammonia in the red solution was also determined. The liquid was warmed, to expel the excess of the volatile alkali, in fact, till there was a distinct odour of iodine. It was then divided into two equal parts, and proceeded with as before. The amount of ammonio-chloride of platinum obtained was 0·723 grm.; that of iodide of silver, as before stated, was 4·376 grms.

These numbers indicate:

Nitrogen . . .	0·0459 grm.
Iodine . . .	2·3572 „

which, divided by the atomic weights, give:

Nitrogen	. 328 or 1	equiv.
Iodine	. 1856 or 5·66	„

There is here a remarkably small amount of ammonia indicated; probably the compound first formed in the red solution is decomposed by a slight heat, the iodide remaining in the liquid, and the ammonia volatilizing.

CHLORIDE OF NITROGEN.

It appeared highly probable that the same methods which had proved applicable to the analysis of the so-called iodide might be effective also when tried with the chloride of nitrogen. The systematic analysis of this oily liquid indeed has never been attempted excepting by Bineau. In the same memoir in which that chemist attributed the correct composition to the iodide, he assigned to the chloride the composition NCl_3.* Since, however, his determinations are far from being exact, doubt might still be entertained as to the actual proportion of the nitrogen and chlorine, and whether the explosive liquid might not, like the iodide, retain some portion of hydrogen. At any rate it would be interesting to try whether the view of Bineau would be confirmed by further experiments, and how far the formula of this substance might throw light upon the rational composition of the iodide.

The so-called chloride of nitrogen was prepared in the usual way, by the mutual action of chlorine and chloride of ammonium. For each separate analysis a globule was collected of just sufficient size; and it was washed by a stream of water until the washings gave no appreciable precipitate with a silver salt. Methods similar to those employed for the decomposition of the iodide were made use of in this case also. A stream of hydrosulphuric acid was passed for a long time through water at the bottom of which was a globule of the explosive liquid. Decomposition took place slowly, sulphur being liberated, and ammonia and hydrochloric acid formed: but at the same time the usual action of water on the compound was proceeding, and thus a little nitrogen gas was produced. This was scarcely more than a trace, but not having been collected, it must have vitiated the experiments to some extent. The solution obtained after this reaction was warmed to expel the excess of hydrosulphuric acid, and filtered from the deposited sulphur. In the first experiment

* Ann. Chim. Phys. [3], XV, 71.

recorded below, the ammonia and hydrochloric acid were determined from the same portion, acetate of silver having been employed to precipitate the latter, excess of silver being subsequently removed by the addition of hydrochloric acid, and the ammonia converted into platinum salt. In the second and third experiments, the solution was divided into two equal parts, from one of which the hydrochloric acid, and from the other of which the ammonia were estimated in the usual manner.

The following are the results:

	Exp. I.	Exp. II.	Exp. III.
Ammonio-chloride of platinum	0·149 grm.	0·082 grm.	0·254 grm.
Chloride of silver	0·226 „	0·138 „	0·510 „

which are equivalent to:

	Exp. I.	Exp. II.	Exp. III.
Nitrogen	0·0092 grm.	0·0052 grm.	0·0161 grm.
Chlorine	0·0544 „	0·0340 „	0·1257 „

These numbers are in the ratio of:

	Exp. I.	Exp. II.	Exp. III.
Nitrogen	1 equiv.	1 equiv.	1 equiv.
Chlorine	2·31 „	2·58 „	3·08 „

The last of these estimations accords with Bineau's formula, but the average of them certainly does not, especially when it is borne in mind that, from the loss of nitrogen in the gaseous form, the chlorine will be overestimated; and thus the smallest proportion of chlorine is probably the truest.

The action of hydrosulphuric acid being evidently not calculated to give an exact means of analysis, sulphurous acid was had recourse to. It was found that a solution of that substance in water acted slowly upon the explosive compound, giving rise to ammonia and hydrochloric acid, with formation of sulphuric acid; a little nitrogen gas was evolved at the same time, but not a trace of nitric acid was formed, as is usually the case when the chloride is left in contact with water. For the purpose of analysis, a globule of the liquid was placed in a small basin, containing a freshly prepared aqueous solution of sulphurous acid, and over it was placed a glass tube also filled with the solution in such a manner that the bubbles of gas all rose into it. After a few hours, the globule had disappeared, a certain amount of nitrogen gas was found, and its volume measured. The solution was warmed to expel the remaining sulphurous acid, and divided

into two equal parts, from one of which the hydrochloric acid, and from the other the ammonia, were estimated in the usual way. The experiment was performed twice, and the following were the results:

	Exp. I.	Exp. II.
Nitrogen gas (divided by 2)	0·04 cub. in.	0·14 cub. in.
Ammonio-chloride of platinum	0·207 grm.	0·122 grm.
Chloride of silver	0·365 „	0·281 „
Sulphate of baryta	0·634 „	0 428 „

which are equivalent to:

	Exp. I.	Exp. II.
Nitrogen	0·0139 grm.	0·0105 grm.
Chlorine	0·0900 „	0·0692 „
Sulphuric acid	0·217 „	0·147 „

These numbers are in the ratio of:

	Exp. I.	Exp. II.
Nitrogen	1 equiv.	1 equiv.
Chlorine	2·56 „	2·60 „
Sulphuric acid	5·47 „	4·89 „

The results of these two experiments almost coincide,* in the proportion of chlorine and nitrogen, and they agree with the average of the experiments by means of hydrosulphuric acid. The proportion between the nitrogen and chlorine is evidently as 1 : 2·5; and as there are 5 equivalents of sulphuric acid formed, it shows that 2·5 equivalents of hydrogen have also been supplied for the production of ammonia. The composition of the explosive chloride therefore is not so simple as that of the so-called iodide: it may be expressed either as a double equivalent of ammonia in which 5 atoms of hydrogen are replaced by iodine, viz., N_2HCl_5; or as $NHCl_2 + NCl_3$.

* There appears a considerable discrepancy between the two estimations of sulphuric acid; but it should be remembered that in such experiments as these, where a solution of sulphurous acid has been exposed for hours to the air, an excess of sulphuric acid may be expected; while on the contrary, the evolution of nitrogen in the gaseous condition, will cause less sulphuric acid to be formed. Hence, no doubt, the deficiency in the second experiment, contrasting so with the excess in the first, where much less gas was produced.

VII.—*On some New Compounds of Salicyl.*

By Charles Gerhardt.

Chemists are aware that the salicylic ethers discovered by M. Cahours, exhibit an anomaly never before observed in compounds of that nature. These ethers, in fact, though they correspond to neutral salicylates, are capable of uniting with bases and forming metallic salts of perfectly definite character. Thus, the salicylate of methyl (oil of *Gaultheria procumbens*) is analogous in composition to salicylate of silver:

$\left.\begin{matrix}C_7H_5O_2\\CH_3\end{matrix}\right\}O$ salicylate of methyl. $\left.\begin{matrix}C_7H_5O_2\\Ag\end{matrix}\right\}O$ salicylate of silver;

nevertheless, the salicylate of methyl combines with potash, soda, baryta, &c.; so likewise does the salicylate of ethyl. In fact these two ethers exhibit the characters of true acids.

The following is another anomaly exhibited by these bodies. When an ordinary ether is treated with chlorine or bromine, the first effect of these agents is always to effect substitutions in the ethylic or methylic elements, in such a manner as to form chloruretted or bromuretted products, which are transformed by alkalies, not into alcohol or wood-spirit, but, as shown by Malaguti, into acetic or formic acid. The salicylic ethers, however, exhibit totally different reactions; for chlorine and bromine, when they act upon these bodies, first attack the salicylic elements, and thus give rise to the formation of the ethers of chlorosalicylic and bromosalicylic acids, &c.

This difference of character being evidently due to difference of molecular constitution, I have been led, in applying my latest theoretical views to the salicylic ethers, to regard them, not as a molecule of water in which the 2 atoms of hydrogen are replaced, the one by salicyl and the other by methyl or ethyl, but as a molecule of water in which only 1 atom of hydrogen is replaced by methylo-salicyl or ethylo-salicyl, that is to say, by salicyl already containing methyl or ethyl in place of hydrogen:

$\left.\begin{matrix}C_7H_4(CH_3)O_2\\H\end{matrix}\right\}O$ hydrate of methylo-salicyl. $\left.\begin{matrix}C_7H_4(C_2H_5)O_2\\H\end{matrix}\right\}O$ hydrate of ethylo-salicyl.

According to this view, salicylate of methyl becomes the hydrate of methylo-salicyl, or the oxide of hydrogen and methylo-salicyl; and salicylate of ethyl becomes the hydrate of ethylo-salicyl, or the oxide of hydrogen and ethylo-salicyl.

Hence it naturally follows, that the compound of salicylate of methyl with potash, for example, is the oxide of potassium and methylo-salicyl:

$$\left.\begin{matrix} C_7 H_4 (C H_3) O_2 \\ K \end{matrix}\right\} O.$$

Now as it is shown by my experiments on the anhydrous acids, that the basic hydrogen in acids, or the metal in salts, may be replaced by oxygenated groups, such as benzoyl, cumyl, ethyl, &c., we ought, if my view of the constitution of the salicylic ethers be correct, to be able to effect corresponding substitutions in these bodies.

This anticipation has been fully confirmed by experiment. Nothing in fact is easier than to *etherify* the salicylic ethers, just as we etherify alcohol or wood-spirit. If, for example, alcohol or wood-spirit be brought in contact with chloride of benzoyl or succinyl, hydrochloric acid is evolved, and benzoate of ethyl, succinate of methyl, &c., is formed. Now, when the salicylic ethers are treated with these same chlorides, a precisely similar reaction takes place, the product being benzoate of ethylo-salicyl or succinate of methylo-salicyl, &c. In a word, we may, with a salicylic ether and the chloride of any acid radical, produce as many compounds as with the same chloride and an alcohol.

All the compounds which I have thus succeeded in preparing, crystallize perfectly.

Benzoate of methylo-salicyl is obtained by causing gaultheria oil and chloride of benzoyl to act on one another with the aid of heat; it crystallizes in beautiful rhomboïdal prisms, containing:

$$\left.\begin{matrix} C_7 H_4 (C H_3) O_2 \\ C_7 H_5 O \end{matrix}\right\} O$$ benzoate of methylo-salicyl, or oxide of benzoyl and methylo-salicyl.

Benzoate of ethylo-salicyl is prepared by a similar process from salicylic ether:

$$\left.\begin{matrix} C_7 H_4 (C_2 H_5) O_2 \\ C_7 H_5 O \end{matrix}\right\} O$$ benzoate of ethylo-salicyl, or oxide of benzoyl and ethylo-salicyl.

Cuminate of methylo-salicyl crystallizes from boiling alcohol in very brilliant rhombic pallets:

$$\left.\begin{matrix} C_7 H_4 (C H_3) O_2 \\ C_{10} H_{11} O \end{matrix}\right\} O$$ cuminate of methylo-salicyl, or oxide of cumyl and methylo-salicyl.

Succinate of methylo-salicyl is obtained by means of the chloride of succinyl lately discovered by M. Chiozza and myself. It is deposited from the alcoholic solution, on cooling, in the form of large rectangular plates, composed of fibres longitudinally attached

but easily separable. It is formed from 2 molecules of water, just like succinic acid, which, as everybody knows, is bibasic:

$$\left.\begin{matrix} C_7H_4(CH_3)O_2 \\ C_7H_4(CH_3)O_2 \\ C_4H_4O_2,\ O \end{matrix}\right\}$$ succinate of methylo-salicyl, or oxide of succinyl and methylo-salicyl.

These examples might be easily multiplied.

I have likewise endeavoured to obtain the chloride of methylo-salicyl by subjecting gaultheria oil to the action of perchloride of phosphorus; but in the very energetic reaction which takes place between these two bodies, the methylo-salicyl group is decomposed, and as products of the action we obtain chloride of methyl and a new chloride, the *chloride of salicyl*.

$$\left.\begin{matrix} C_7H_5O_2 \\ Cl \end{matrix}\right\}$$ chloride of salicyl.

This body must not be confounded with that to which M. Piria has given the same name, and which, in my opinion, represents the hydride of chloro-salicyl. My chloride of salicyl is a fuming liquid, which is decomposed by water, like the chlorides of silicium, phosphorus, ethyl, &c., into hydrochloric and salicylic acids. It acts violently on alcohol and wood-spirit, converting them into salicylic ethers. This chloride of salicyl likewise affords a means of preparing salicylate of ethyl much more readily than from a mixture of alcohol, salicylic acid, and sulphuric acid. M. Drion, who is pursuing in my laboratory the study of the newly discovered compounds above mentioned, has also, by means of this new chloride of salicyl, obtained the *salicylate of amyl*, which several chemists have in vain attempted to produce by the methods hitherto known.

This salicylate of amyl exhibits characters similar to those of the other salicylic ethers; it may evidently be regarded as the hydrate of amylo-salicyl:

$$\left.\begin{matrix} C_7H_4(C_5H_{11})O_2 \\ H \end{matrix}\right\}O$$ hydrate of amylo-salicyl.

When treated with chloride of benzoyl, it yields *benzoate of amylo-salicyl*.

$$\left.\begin{matrix} C_7H_4(C_5H_{11})O_2 \\ C_7H_5O \end{matrix}\right\}O$$ benzoate of amylo-salicyl.

This body crystallizes in splendid needles.

The preceding results are in perfect harmony with the theoretical views advanced in my most recent publications.

VIII.—*On the existence of Trimethylamine in the brine of salted herrings.*

By Gersham Henry Winkles.

In the second memoir of Dr. Hofmann's "Researches into the Molecular Constitution of Organic Bases," published in the Philosophical Transactions for 1851, we find, at page 392, the following note on Propylamine:

"M. Wertheim, the discoverer of this base, believes that it stands to the unknown propyl-alcohol* in the same relation which exists between methylamine, ethylamine, and amylamine on the one hand, and methylic, ethylic, and amylic alcohol on the other. It deserves, however, to be noticed that the formula C_6H_9N for this compound, as determined by experiment, expresses not only propylamine, but also trimethylamine and even methyl-ethylamine:

$$C_6H_9N=\left\{\begin{matrix}H\\H\\C_6H_7\end{matrix}\right\}N=\left\{\begin{matrix}C_2H_3\\C_2H_3\\C_2H_3\end{matrix}\right\}N=\left\{\begin{matrix}H\\C_2H_3\\C_4H_5\end{matrix}\right\}N$$

In the absence of decisive reactions, it remains doubtful which of these formulæ represents the base obtained by the action of soda-lime on narcotine. I may state here, that propylamine, as prepared by Wertheim's process, and the liquid containing trimethylamine—for as yet I have not obtained this substance perfectly pure—exhibit the same remarkable fishy odour. It deserves, moreover, to be remarked that Dr. Anderson found that propylamine occurs, associated with methylamine, among the basic products of the decomposition of codeine."

To remove the doubts which existed in regard to the formula of the above-mentioned base C_6H_9N, I undertook, at the request of Dr. Hofmann, the following investigation.

The first consideration was, how and from whence to obtain the base in a state of purity and in sufficient quantity for the necessary experiments. Besides the two sources mentioned in Dr. Hofmann's note, viz. the action of soda-lime on narcotine and the decomposition of codeine, Wertheim detected its presence in the decomposition of fishy matter; I therefore resolved to look for it in the ordinary salted herrings, or rather in the brine in which they arrive here from the coasts of Scotland and other fishing stations.

* The propyl-alcohol has been since discovered by M. Chancel.

This brine, consisting of salt, portions of broken fish, roe, &c., is collected by the retail dealers in London, and sold, in barrels of about 4 cwts. each, to the manufacturers of anchovy sauce, in the preparation of which it is largely used.

Propylamine being, according to Wertheim, of a highly inflammable nature, I found no difficulty in detecting its presence. A small portion of the brine was acidified with hydrochloric acid, evaporated to dryness, and the residue introduced into a test-tube together with potassa, and heated. A powerful odour of ammonia was given off, and on approaching a lighted taper, the evolved gases burnt freely at the mouth of the tube. The presence of the base, or of some similar bases, being thus established, I was now able to proceed on a larger scale.

The contents of one barrel, about 26 gallons by measure, were acidified with crude hydrochloric acid; filtered; and the filtrate evaporated nearly to dryness; distilled with lime; the distillate again acidified, evaporated, and distilled with potassa, thus getting rid of all the nauseous fish-oils obtained in the first process. The distillate was again acidified with hydrochloric acid, and evaporated down as far as the hygroscopic nature of the salts permitted, then treated with absolute alcohol, and filtered in order to remove the large quantity of chloride of ammonium present.

After distilling off all the alcohol, sticks of potassa were introduced into the retort, and the anhydrous bases condensed in a cooling apparatus. During this operation, a large quantity of uncondensed inflammable gas passed through the two-necked receiver, and was absorbed by water.

The condensed liquid proved to be a mixture of several bases, at least of four, the boiling-point commencing at 35° C. and rising to 140°, remaining somewhat stationary at various intermediate points; but as the substance prepared was not sufficient for the experiments, I proceeded at once with a second cask of herring-salt, and by following a process recommended by Mr. Warren Delarue, avoided the trouble and the great loss of time and substance, which I had before experienced.

The brine, together with some lime, was put into a copper-still, having an ordinary worm-tub as condensor; a pipe connected with a large steam-boiler, and open at the end, was passed through the lid to the bottom of the still. By this arrangement steam at a high pressure was forced through the mixture of herring-salt and lime, carrying with it all the volatile products set free by the alkali.

The first six gallons of this distillate being an aqueous solution of the bases, was acidified with hydrochloric acid, evaporated, and treated with absolute alcohol in the same manner as the first portion.

And here I should mention that chloride of ammonium, though slightly soluble in absolute alcohol, seemed to lose that solubility in the presence of the hydrochlorates of the bases for which I was in search, as I could not detect a trace of ammonia in any of the further manipulations.

After evaporating the alcohol, the concentrated aqueous solution of the hydrochlorates was gradually introduced by means of a safety-tube into a retort filled with caustic lime, the heat arising from the decomposition being sufficient to carry on the distillation without the aid of a gas-flame.

The less volatile bases, condensed as usual, were collected in a two-necked receiver; the more volatile passed from thence through several U-tubes immersed in a strong freezing mixture, a form of apparatus by means of which, a few days previously, Dr. Hofmann had succeeded in preparing trimethylamine.

Long before any trace of liquid could be observed in the globe-receiver, the U-tubes were filled with a clear, colourless, transparent fluid, which had to be removed several times before the distillation was complete.

In this way I obtained more than a quarter of a pint of anhydrous base, which had to be kept under ice in order to preserve it.

Only a small quantity of the less volatile bases was obtained, even at a high temperature; in appearance they were the same as obtained from the first operation. But as yet I have not been able to study them, the more volatile ones claiming my immediate attention.

The boiling point of this interesting body lies between 4° and 5° C., corresponding exactly to that of trimethylamine, as obtained from the decomposition of the oxide of tetramethylammonium by heat: in appearance and odour no difference can be perceived.

Water or alcohol absorbs this base as rapidly as it does ammonia, and mixed with about one-half its volume of water I have been able to keep it; mixed with its own bulk of water, it still retains its inflammability, burning like ether.

It is powerfully alkaline: neutralised with hydrochloric acid it forms a very deliquescent salt, which with bichloride of platinum forms a magnificent double salt, crystallizing in orange-coloured octahedrons.

On analysis, the following results were obtained:

·3125	grm. of	platinum-salt	gave	·1165	grm. of platinum.
·3530	„	„	„	·1315	„ „
·3680	„	„	„	·1805	„ carbonic acid.
„	„	„	„	·1250	„ water.

	Percentage.	
Platinum . . .	37·28	37·25
Carbon	13·377	
Hydrogen . . .	3·776	

The following theoretical values correspond to the formula

$$C_6 H_9 N, HCl, Pt Cl_2$$

		Theory.		Experiment.
6 equivs.	carbon . .	36·00	13·575	13·377
10 „	hydrogen . .	10·00	3·771	3·776
1 „	nitrogen . .	14·00	5·279	
3 „	chlorine . .	106·50	40·161	
1 „	platinum . .	98·68	37·214	37·265
		265·18	100·000	

Having thus obtained the substance, corresponding in composition, &c., to Wertheim's propylamine, I proceeded to determine the constitution.

On examining the above-given formulæ:

$$\left.\begin{matrix} C_2 H_3 \\ C_2 H_3 \\ C_2 H_3 \end{matrix}\right\} N \qquad \left.\begin{matrix} H \\ C_2 H_3 \\ C_4 H_5 \end{matrix}\right\} N \qquad \left.\begin{matrix} H \\ H \\ C_6 H_7 \end{matrix}\right\} N$$

it will readily be seen that, in order to produce a base corresponding in its reactions to the oxide of Dr. Hofmann's fourth class compound ammonias, we should have to substitute respectively, one, two, or three equivalents of an alcohol-radical; by this method of proceeding the correct formula must at once be ascertained.

On adding iodide of methyl to a few drops of anhydrous base, combination took place instantaneously, giving rise to explosions and intense heat, the white solid thus formed in the test-tube being ejected with violence. By diluting the base with water, or better with alcohol, previous to adding iodide of methyl, the action takes place in a more quiet manner.

After heating the resulting iodide, in order to remove the excess

of iodide of methyl present, it was dissolved in boiling water, from which it separated again on cooling in beautiful white rectangular prismatic crystals.

Analysis of this salt, dried at 100° C., gave the following results:

·7512 grm. of iodide of the base gave ·8813 of iodide of silver.
·4138 „ „ „ ·3626 „ carbonic acid.
„ „ „ „ ·2237 „ water.

	Percentage.
Iodine . . .	63·425
Carbon . . .	23·89
Hydrogen . .	6·00

The following theoretical values correspond to the formula:

$$C_8\,H_{12}\,N\,I = \left.\begin{matrix} C_2\,H_3 \\ C_2\,H_3 \\ C_2\,H_3 \\ C_2\,H_3 \end{matrix}\right\} N\,I.$$

		Theory.		Experiment.
8 equivs. of carbon		48·00	23·869	23·89
12 „	hydrogen	12·00	5·967	6·00
1 „	nitrogen	14·00	6·962	
1 „	iodine	127·10	63·202	63·425
		201·10	100·000	

On adding to an aqueous solution of the iodide some potash, the iodide separated unaltered, being less soluble in a solution containing that alkali than in pure water.

Oxide of silver added to the solution of the above salt removed the iodine as iodide of silver, without the evolution of any volatile substance, even on ebullition, the solution becoming strongly alkaline.

These two reactions prove that the base found in decomposed fishy matter is trimethylamine, and not propylamine as supposed by Wertheim.

An analysis of the platinum-salt formed by the addition of hydrochloric acid and bichloride of platinum to the oxide liberated by oxide of silver as above, gave the following results:

I. ·1838 grm. of platinum-salt gave ·0644 grm. of platinum
II. ·3266 „ „ ·1148 „ „
·3675 „ „ ·2420 „ carbonic acid
„ „ „ ·1495 „ water.

	Percentage.	
Platinum . . .	35·04	35·15
Carbon	17·96	
Hydrogen . . .	4·57	

The following values correspond to the formula:

$$C_8 H_{12} N Cl, Pt Cl_2 = \left.\begin{matrix} C_2 H_3 \\ C_2 H_3 \\ C_2 H_3 \\ C_2 H_3 \end{matrix}\right\} N Cl, Pt Cl_2$$

		Theory.		Experiment.
8 equivs. of carbon		48·00	17·193	17·96
12 „	hydrogen	12·00	4·298	4·57
1 „	nitrogen	14·00	5·015	
3 „	chlorine	106·50	38·144	
1 „	platinum	98·68	35·350	35·10
		279·18	100·000	

IX.—*On the Action of Iodide of Ethyl on Toluidine.*

By Reginald I. Morley and John S. Abel,
Assistants in the Royal College of Chemistry.

Chemists are acquainted with the results obtained by Dr. Hofmann in his researches on the organic bases, which led him to establish the existence of four groups of bases derived from ammonia, by the replacement of its several hydrogen equivalents by organic radicals. He pointed out at the same time a simple method of ascertaining in what group an organic base has to be classified. This method, as is well known, consists in treating the substance under examination with the iodide of an alcohol radical.

The experiments to which we are about to refer, undertaken at

his invitation, and carried out under his kind superintendence, refer to the examination in this direction of an organic base which has repeatedly claimed the attention of the faculty—viz., Toluidine. The origin of this body, derived step by step from toluylic acid, toluol, and nitrotoluol, places the substance on the same line with the aniline, the formation of which from benzoic acid, benzol, and nitrobenzol is well known. The perfect homology of toluidine and aniline is moreover unequivocally proved by their physical properties. The constitution of aniline has been established, it may be said, beyond any doubt: it has been proved that in its salts the substance may be received as ammonium in which 1 equiv. of hydrogen is replaced by 1 equiv. of the hydrocarbon, $C_{12}H_5$, to which the name of Phenyl has been given, or in the free state as ammonia, 1 equiv. of hydrogen of which is replaced by the same radical.

Salts.		Free Bases.	
Chloride ammonium	$\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}$ N Cl	Ammonia	$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}$ N
Aniline salt	$\left.\begin{matrix}H\\H\\H\\C_{12}H_5\end{matrix}\right\}$ N Cl	Aniline	$\left.\begin{matrix}H\\H\\C_{12}H_5\end{matrix}\right\}$ N

If toluidine is a perfect homologue of aniline, its constitution must be perfectly similar; so that if the latter has in fact this constitution, toluidine must be represented by the formula

$$\left.\begin{matrix}H\\H\\C_{14}H_7\end{matrix}\right\} N,$$

when it becomes ammonia in which 1 equiv. of hydrogen is replaced by toluyl, $C_{14}H_7$; and it is this constitution which has been assumed by Dr. Hofmann in his papers on the bases. It remained to verify this assumption experimentally. This verification forms the subject of the present communication. We rapidly pass over the preparation of toluol from coal naphtha, although we had to perform an immense number of distillations, until the hydrocarbon at last boiled stationary at 111° C. (231°·8 F.) The conversion of toluol into nitrotoluol is attended with difficulties: heat must be carefully avoided, otherwise a considerable quantity of

dinitrotoluol is produced, which forms far more readily than dinitrobenzol. The reduction of nitrotoluol by means of sulphuretted hydrogen, lastly, is an operation tedious in the extreme; it can be accomplished only by a series of supersaturations and distillations. The purification of the toluidine was effected in the form of oxalate. On account of the facility with which it was obtained, we selected from among the alcohol-iodides, iodide of ethyl as the substance to the action of which the toluidine was to be submitted.

We now proceed to describe the results obtained in this reaction.

ETHYLOTOLUIDINE.

A portion of the toluidine was sealed up in a tube with excess of iodide of ethyl, and exposed to the temperature of the water-bath for two or three days. The toluidine mixed with the iodide, and the whole became one crystalline mass; towards the latter part, however, an oily layer separated on the upper surface of the liquid. The tube was now opened, and the excess of iodide of ethyl distilled off in a water-bath, when iodide of ethylotoluidine remained as a heavy oil possessing a peculiar alliaceous smell; this oil was decomposed by distillation with a strong solution of potassa at a high temperature, when a colourless oil distilled over, lighter than water, and possessing a peculiar odour. This oil, the new base, was separated from the water with which it had distilled over, and dried over stick potash. When thus rectified, its boiling point was found to be 217° C. (422°·6 F.), the spec. grav. being 0·9391 at 15°·5 C. (60° F.)

From the comparison of the boiling points of aniline, (about 180° C.), and toluidine (200° C.), we might have expected that by the introduction of 4 equivs. of carbon and hydrogen into the latter base, its boiling point would have been raised about 40° C. It appears, however, that this rule does not hold good in all cases of this kind, Dr. Hofmann having observed a similar comportment with ethylaniline.

Platinum-salt of Ethylotoluidine.—This was at first prepared by adding excess of hydrochloric acid to the liquid from which the base had been separated, and which possessed a strong alkaline reaction. The hydrochlorate thus formed was evaporated on a water-bath, until, when mixed with bichloride of platinum, the double salt crystallized on cooling. In this manner a considerable quantity of a fine crystalline salt was obtained, soluble in water, and, when washed with alcohol, of a pale yellow colour. For analysis, a portion of the crystals was

dried in the water bath, until the weight was constant, and burnt as usual. The quantity of platinum obtained was slightly too large for ethylotoluidine; a circumstance which we explained by the possible presence of a trace of toluidine in the liquid from which the salt was prepared.

An attempt to recrystallize the salt only resulted in the total loss of our substance by decomposition; a fresh portion of hydrochlorate was prepared from some of the base, evaporated, and mixed with bichloride of platinum; a precipitate was formed which dissolved in excess of the bichloride, from which solution the salt could not again be obtained. It was necessary, therefore, to add the platinum solution very cautiously, and when the precipitate was formed, alcohol was added, which dissolved the salt, but again deposited it on agitation after a short time. In this manner, with much trouble, sufficient platinum-salt was prepared for another determination. The double salt being very soluble in alcohol, it was washed with ether; it was found to decompose at 100° C. As the colour became darker, and no constant weight could be arrived at, it was dried for analysis *in vacuo* over sulphuric acid.

0·1580 grm. of platinum-salt gave
0·0460 „ platinum = 29·11 per cent.

According to the formula $C_{18} H_{13} N$, H Cl, Pt Cl_2, or

$$\left.\begin{matrix} C_{14} H_7 \\ C_4 H_5 \\ H \\ H \end{matrix}\right\} N\,Cl, Pt\,Cl_2$$

the percentage of platinum should be 28·93 per cent. The difference is 0·08.

Our next step was to confirm the composition of the base by a determination of the carbon and hydrogen. The platinum-salt being so difficult to obtain, we burnt the base itself, which, as it darkens on keeping, like aniline, toluidine, &c., was redistilled for this purpose.

0·1425 grm. of substance gave
0·4175 „ carbonic acid
0·1255 „ water,

leading to the following percentages,

Carbon . . .	79·90
Hydrogen . . .	9·78

The formula

$$\left.\begin{matrix} C_{14}\,H_7 \\ C_4\,H_5 \\ H \end{matrix}\right\} N = C_{18}\,H_{13}\,N$$

requires the following values:

		Theory.		Experiment.
18 equivs. of carbon	. .	108 =	80·00	79·90
13 „ hydrogen	.	13 =	9·63	9·78
1 „ nitrogen	.	14 =	10·37	
		135	100·00	

These numbers sufficiently establish the composition of ethylotoluidine. Ethylotoluidine forms crystalline compounds with oxalic and sulphuric acids.

DIETHYLOTOLUIDINE.

A portion of the ethyl-base was next sealed up with an excess of iodide of ethyl, and exposed for two or three days to the temperature of boiling water, in order to produce diethylotoluidine. After that time, on allowing the tube to cool and gently agitating it, beautiful crystals of the iodide of the new base at once formed throughout the whole length of the liquid, which dissolved again on placing the tube in the water bath. The excess of iodide of ethyl was again separated as before, when the iodide of diethylotoluidine remained in the flask, from which it crystallized in fine six-sided prisms, so soluble in water that they could scarcely be crystallized from it. The salt separated from the aqueous solution in oily drops, which assumed the crystalline form on being touched with a glass rod. It appeared to be decomposed by alcohol, as also by continued exposure to the atmosphere. For analysis, some of the recrystallized salt was dried *in vacuo* over sulphuric acid (the crystals having been found to decompose in the water bath), dissolved in water, and the iodine determined by precipitation with nitrate of silver in the usual manner.

0·3130 grm. of iodide gave
0·2520 „ iodide of silver,

orrespo nding to percentage of iodine, 43·45. The formula

$$\left.\begin{matrix} C_{14}\,H_7 \\ C_4\,H_5 \\ C_4\,H_5 \end{matrix}\right\} N, HI = C_{22}\,H_{18}\,N, I,$$

requires 43·66 per cent. of iodine; thus proving the crystals to have the above composition.

The remainder of the salt was distilled with potash, and the base thus obtained on the surface of water, from which it was separated. Diethylotoluidine is colourless, and possesses a smell like the former compound. After rectification from potash it was found to boil at 229° C. (444°·2 F.), thus showing another deviation from the rule. Its spec. grav. at 15°·5 C. (60° F.) was 0·9242.

The preparation of the platinum-salt of this base presented insurmountable difficulties: it could not be obtained otherwise than as a resinous mass, to crystallize which all attempts were abortive.

A combustion of the base was however made:

0·1495 grm. of substance gave
0·4435 „ carbonic acid,
0·1410 „ water,

leading to the following percentages:

Carbon	80·90
Hydrogen	10·47

The formula

$$\left.\begin{matrix} C_{14}\,H_7 \\ C_4\,H_5 \\ C_4\,H_5 \end{matrix}\right\} N = C_{22}\,H_{17}\,N$$

requires the following values:

	Theory.		Experiment.
22 equivs. of carbon . .	132	80·98	80·90
17 „ hydrogen .	17	10·43	10·47
1 „ nitrogen .	14	8·59	
	163	100·00	

The results obtained correspond therefore sufficiently with the above formulæ.

OXIDE OF TRIETHYLOTOLUYLAMMONIUM.

It now remained for us to convert the volatile into a fixed base, similar to those which Dr. Hofmann has distinguished by the laboratory term ammonium-bases. The formation of such a substance by the introduction of another equivalent of $C_4\,H_5$ into diethylotoluidine would establish beyond any doubt the perfect homology of aniline and toluidine.

This new base might be called oxide of triethylotoluidine or oxide of triethylotoluylammonium.

For this purpose we again sealed up the last base with iodide of ethyl, and exposed the tube to a temperature of 100° C. (212° F.) for some days, till fine prismatic crystals of an iodide had formed in the solution. After distilling off the excess of iodide of ethyl as before, the iodide of the new base remained as a heavy oil: this was decomposed by heating with freshly precipitated oxide of silver, when the liberated oxide of triethylotoluylammonium at once entered into solution, leaving iodide of silver. The solution after filtration was found to possess an extremely bitter taste, and to be very alkaline to test-paper. With salts of the metallic oxides, a solution of this base behaved in most cases similarly to potash and to Dr. Hofmann's oxide of tetrethylammonium: thus, with salts of baryta, strontia, lime, and magnesia, a white precipitate insoluble in excess was formed.

The following is a list of the reactions of this substance:

Barium-salts.—White precipitate of the hydrate of the earth, insoluble in an excess of the base.

Strontium-salts.—White precipitate of the hydrate of the earth, insoluble in an excess of the base.

Calcium-salts.—White precipitate of hydrate of the earth, insoluble in excess of the base.

Magnesium-salts.—White precipitate of hydrate of the earth, insoluble in an excess of the base.

Aluminum-salts.—White gelatinous precipitate soluble in large excess of the base.

Chromium-salts. — Green hydrated sesquioxide insoluble in excess.

Nickel-salts.—Green protoxide insoluble in excess.

Cobalt-salts.—Pink hydrate of protoxide insoluble in excess.

Manganese-salts. — Whitish hydrated protoxide insoluble in excess.

Salts of Protoxide of Iron.—Green hydrated protoxide insoluble in excess.

Salts of Sesquioxide of Iron.— Brown hydrated sesquioxide insoluble in excess.

Zinc-salts.—Hydrate of the protoxide soluble in excess.

Lead-salts.—White hydrate of protoxide soluble in excess.

Silver-salts.—Brown protoxide insoluble in excess.

Salts of Suboxide of Mercury.—Black suboxide insoluble in excess.

Salts of Protoxide of Mercury.—White precipitate insoluble in excess.

Copper-salts.—Blue hydrated protoxide insoluble in excess, becoming black by ebullition.

Cadmium-salts.—White hydrated protoxide insoluble in excess.

Bismuth-salts.—White hydrated teroxide insoluble in excess.

Antimony-salts, Teroxide.—White hydrated teroxide soluble in excess.

Salts of Protoxide of Tin.—White hydrated protoxide soluble in excess.

Salt of Binoxide of Tin.—White hydrated binoxide soluble in excess.

Gold-salts.—Yellow precipitate of the double salt.

Platinum-salts.—Yellow precipitate of the double salt.

Platinum-Salt.—When the chloride of this base was mixed with bichloride of platinum, a copious precipitate of a fine crystalline platinum-salt was produced, which was nearly insoluble in cold water, but was dissolved readily in hot water, from which solution it crystallized in beautiful needles.

The salt was thrown upon a filter, washed and dried at 100° C.

Both the original and crystallized salts were analyzed.

I. 0·1640 grm. of platinum-salt gave on ignition
0·0410 „ platinum.

II. 0·6100 grm. of platinum-salt gave on ignition
0·1515 „ platinum.

	Theoretical percentage.	Experimental percentage.
Platinum . .	24·85	24·91

Recrystallized salt.

0·5212 grm. of platinum-salt gave on ignition
0·1292 „ platinum.

	Theory.	Experiment.
Platinum .	24·85	24.5

It appears, therefore, that this platinum-salt, like some observed by Dr. Hofmann, loses platinum by recrystallization.

For combustion, some of the original salt was employed.

0·5300 grm. of platinum-salt gave
0·7600 „ carbonic acid,
0·2690 „ water, and
0·1310 „ platinum.

The numbers required by the formula

$$\left.\begin{matrix} C_{14}\,H_7 \\ C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \end{matrix}\right\} N\,Cl,\,Pt\,Cl_2 = C_{26}\,H_{22}\,N\,Cl,\,Pt\,Cl_2,$$

are shown in the following table, together with the numbers obtained by experiment, from which it will be seen that little doubt can remain as to the formula of the salt analyzed.

		Theory.		Experiment.
26 equivs. of carbon		156	39·27	39·11
22 „	hydrogen	22	5·54	5·64
1 „	nitrogen	14	3·52	
1 „	platinum	98·7	24·85	24·71
3 „	chlorine	106·5	26·82	
		397·2	100 00	

These experiments establish the existence of the following bases, which we place in juxtaposition with those of the homologue phenyl.

Phenylamine	$\left.\begin{matrix} H \\ H \\ C_{12}\,H_5 \end{matrix}\right\} N$	Toluylamine	$\left.\begin{matrix} H \\ H \\ C_{14}\,H_7 \end{matrix}\right\} N$
Aniline		Toluidine	
Ethylaniline	$\left.\begin{matrix} H \\ C_4\,H_5 \\ C_{12}\,H_5 \end{matrix}\right\} N$	Ethylotoluidine	$\left.\begin{matrix} H \\ C_4\,H_5 \\ C_{14}\,H_7 \end{matrix}\right\} N$
Diethylaniline	$\left.\begin{matrix} C_4\,H_5 \\ C_4\,H_5 \\ C_{12}\,H_5 \end{matrix}\right\} N$	Diethylotoluidine	$\left.\begin{matrix} C_4\,H_5 \\ C_4\,H_5 \\ C_{14}\,H_7 \end{matrix}\right\} N$
Triethylaniline	$\left.\begin{matrix} C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \\ C_{12}\,H_5 \end{matrix}\right\} N$	Triethytoluidine	$\left.\begin{matrix} C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \\ C_{14}\,H_7 \end{matrix}\right\} N$

In conclusion, we may observe that the combustion of this pla-

tinum-salt, as well as all the combustions made in the course of this investigation, were performed in Dr. Hofmann's new gas furnace for organic analysis. It deserves to be mentioned, that to ensure complete combustion, the liquids were weighed in small open tubes filled with oxide of copper and a little powdered chlorate of potassa, the oxygen of which, expelled with the last stage of the process, ensured the complete combustion of any small particles of carbon that might otherwise have remained unconsumed.

X.—*On Red Prussiate of Potash.*

By William Wallace.

During the present winter I have been engaged with a series of experiments on the yellow and red prussiates of potash. In the present notice I propose to communicate the results obtained on the following points: 1st, the oxydizing power of ferricyanide of potassium in presence of potash; 2nd, the analysis or valuation of commercial red prussiate of potash; and 3rd, the solubility of ferricyanide of potassium in water at different temperatures.

Oxydizing Power.—The oxydizing power of ferricyanide of potassium, especially in presence of an alkali, has been investigated by several chemists, particularly by Schönbein* and by Boudalt.† The results of my experiments confirm in general those described by Schönbein and others, but in a few cases differences were observed. Several reactions of considerable interest have likewise been added. The action in all cases consists in the conversion of ferricyanide of potassium into ferrocyanide by the absorption of one equivalent of potassium.

In the experiments here referred to, a certain amount of free alkali was invariably present, and the mixtures were generally heated, and when necessary, boiled. The ferrocyanide of potassium produced was obtained in crystals by evaporation, or by the addition of alcohol.

Of non-metallic elementary bodies, iodine was converted into iodic acid, sulphur into sulphuric acid, and phosphorus into phosphoric acid, the latter very slowly. Hydrogen gas was not oxydized.

Of the metals, iron, zinc, bismuth, lead, tin, arsenic, and antimony,

* J. pr. Chem. XX, 128. † Ibid. XXX, 23.

were rapidly oxydized, but copper and mercury were not sensibly affected. In all cases in which the resulting oxides were soluble in potash, the ferricyanide was rapidly and completely converted into ferrocyanide, the liquid becoming nearly colourless.

Of non-metallic compounds, binoxide of nitrogen was converted into nitric acid, sulphurous and hyposulphurous acids into sulphuric acid (the latter with difficulty), and oxalic acid into carbonic acid.

Of metallic oxides, the protoxides of iron, manganese, cobalt, nickel, lead, and tin, were raised to the state of peroxides, the suboxides of copper and mercury to protoxides, sesquioxide of chromium to chromic acid, oxide of antimony to antimonic acid, and arsenious acid to arsenic acid. The protoxides of zinc and bismuth were not altered. The experiments were performed by mixing ferricyanide of potassium with a salt of the oxide, warming the mixture, and then adding potash in excess.

Of other inorganic compounds, sulphide and iodide of potassium gave up their metal to the ferricyanide, with separation of sulphur and iodine, the sulphide and iodide being present in excess. The sulphur and iodine were dissolved by the potash, but were precipitated on neutralizing the liquid with an acid. A similar action occurred with the sulphides of the heavy metals, especially with those which are soluble in potash. Cyanide of potassium was converted into cyanate of potash.

Most organic compounds which are not of a very stable nature are more or less readily oxidized by ferricyanide of potassium in presence of free alkali. A solution of ferricyanide, with potash, boiled with sugar in excess, was rapidly and completely converted into ferrocyanide, the sugar being oxidized to carbonic acid and water. A similar action was observed to occur with gum, starch, dextrin, and paper, but much less readily than with sugar. When alcohol was treated in the same manner, the greater part of the salt was rapidly converted into ferrocyanide; but a portion was decomposed, with probable formation of cyanate of potash, sesquioxide of iron having been precipitated. The alcohol seemed to be converted into carbonic acid and water.

In the arts, ferricyanide of potassium has been employed for discharging or bleaching indigo and the colouring principles of cochineal and lac-dye. It also destroys litmus, turmeric, and many other colours, but does not bleach them completely.

Valuation of Commercial Red Prussiate of Potash.—This salt is met with in commerce in two states, viz., in crystals and in powder. The latter variety is sometimes prepared by grinding the crystals, but more frequently by exposing finely-pulverized ferrocyanide of potassium to the action of chlorine gas. The product is a mixture of ferricyanide and chloride of potassium. In its preparation, a portion at least of the water of crystallization of the ferrocyanide must be retained, for the dry salt is very little affected by dry chlorine gas; consequently the product, unless purposely dried, must always be contaminated with a certain proportion of water. The chloride of potassium and water were found to amount to about 22 per cent of the powder when freshly prepared. Besides these, there may exist accidental impurities, arising from the employment of impure ferrocyanide, a deficiency of chlorine, and other circumstances; and it might also be largely adulterated with common salt, without materially influencing its appearance. A simple and ready method of estimating its value is therefore of some importance.

Mr. Lieshing* has recently published a very elegant process for the estimation of the amount of pure ferricyanide in the commercial product. He converts the salt into ferrocyanide by the action of sulpharseniate of sodium; but as this reagent is difficult to prepare, the application of Mr. Lieshing's method must necessarily be limited.

Many substances capable of being easily oxidized were tried with the same object, but protochloride of tin in presence of hydrochloric acid was found to be most suitable. The process about to be described is confidently recommended as being exceedingly simple, and as yielding very accurate results. It is based upon the well-known reducing power of proto-compounds of tin; and the tendency which ferricyanide of potassium has to combine with an additional equivalent of alkali-metal, or of hydrogen, forming ferrocyanide of potassium and hydroferrocyanic acid. The decomposition may be thus represented:

$$2\,(K_3Fe_2Cy_6) + 2\,HCl + 2SnCl = 3\,(K_2FeCy_3) + H_2FeCy_3 + 2\,SnCl_2.$$

A large excess of hydrochloric acid is added, in order to prevent the formation of ferrocyanide of tin. The action is immediate, and takes place at ordinary temperatures.

100 grains of the sample of red prussiate under examination are dissolved in an ounce and a half of water, and three quarters of an ounce of strong hydrochloric acid are added. An alkalimeter is filled with a solution of chloride of tin, having a specific gravity of about

* Chem. Soc. Qu. J. April, 1853.

1·046, and containing in 100 measures about 35·7 grains of tin. The tin solution is added to that of the red prussiate, until the latter loses the green colour that it acquires, and becomes of a bright and distinct violet, or blue tint, without the slightest shade of green. The exact point at which this effect occurs is easily ascertained by placing a drop of the liquid on a slab, after each addition of the tin liquor. The blue colour of the solution is owing to a slight decomposition of the hydroferrocyanic acid produced during the action. A similar experiment is performed with 100 grains of pure and dry ferricyanide of potassium, and the amount of pure salt in the sample is then obtained by a simple calculation.

It was found very convenient to employ a standard solution of chloride of tin, of which each division is equal to 1 or 2 grains of pure ferricyanide. This solution may be preserved without material alteration for a considerable period, if kept in a properly closed vessel.

The accuracy of the process depends upon the extensive colouring power of ferricyanide of potassium. Its solution in 7,000 parts of water is distinctly yellow when spotted upon a slab, and communicates a great tint to blues. In the process just described, a distinct green colouration is observed if 0·2 of a grain of the salt remain unchanged in the solution.

Solubility of Ferricyanide of Potassium.—Gmelin states that this salt requires for solution 3·8 parts of cold water, and a smaller proportion of hot water; while Girardin affirms that is soluble in 2 parts of cold, and in less than 1 part of hot water. Its solubility at various temperatures has been carefully determined. The results obtained are stated in the following table, which likewise exhibits the specific gravity of the solutions at the temperatures mentioned, compared with water at 60° F.

Temperature.	Sp. gr.	Soluble in parts water.	100 parts of water dissolve
40°	1·151	3·03	33·0
50	1·164	2·73	36·6
60	1·178	2·54	40·8
100	1·225	1·70	58·8
212	1·250	1·29	77·5
220	1·265	1·21	82·6

220° is the boiling-point of the saturated solution. The specific gravity of the salt itself is 1·845.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

January 16, 1854.

Colonel Philip Yorke, President, in the Chair.

The following donations were announced:

"Journal of the Franklin Institute for December, 1853:" from the Franklin Institute.

"Pharmaceutical Journal for January, 1854:" from the Editor.

"Report of the Council of the Art Union of London:" from the Art Union.

"Journal of the Society of Arts:" 2 numbers, from the Society of Arts.

"Literary Gazette:" 2 numbers, from the Publishers.

"Bericht über die Verhandlungen der naturforschenden Gesellschaft in Basel, von August, 1850, bis Juni, 1852."

Henry J. Smith, Esq., B.A., Fellow and Tutor of Baliol College, Oxford; George Payne, Esq., of Vauxhall; The Rev. John H. Molesworth St. Aubin, M.A., of Clowance Park,

Cornwall; and Samuel Highley, Jun., Esq., 32, Fleet Street, were duly elected Fellows of the Society.

The following papers were read:

1. "On some new Compounds of Salicyl," by Charles Gerhardt: communicated by Dr. Williamson.
2. "On Red Prussiate of Potash," by William Wallace: communicated by Dr. F. Penny.

February 6, 1854.

Colonel Philip Yorke, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:

C. De Bussy, Esq., University College;
David Evans, Jun., Esq., Crayford; and
Arthur W. Wills, Esq., Edgbaston, Birmingham.

A resolution of the Council was read, recommending to the Society that the names of seven Fellows, whose subscriptions were greatly in arrear, be removed from the list of Fellows, in accordance with the Bye-laws of the Society.

The following papers were read:

1. "On the existence of Trimethylamine in the Brine of Salted Herrings:" by Gersham Henry Winkles: communicated by Dr. Hofmann.
2. "On the Action of Iodide of Ethyl on Toluidine:" by Reginald I. Morley and John S. Abel.

February 20, 1854.

COLONEL PHILIP YORKE, President, in the Chair.

The following donations were announced:

"Chemical Analysis of the Water of Holywell, Tadmarton Heath, with an inquiry as to its fitness for the water supply of the town of Banbury:" by Thomas Busby, F.C.S.

"Bulletins des Séances de la Classe des Sciences:" Bruxelles, 1852.

"Ueber die Beschaffenheit der Lava des Aetna von der Eruption im Jahre 1852:" von Karl Ritter von Hauer, K. K. Hauptmann.

"Untersuchung von Ackererden aus dem Banate:" von Rudolph Ritter von Hauer.

"Chemische Analyse der Fahlerze von Poratsch, bei Schmölnitz, in Ungarn:" von C. Ritter von Hauer, 1852.

"Bulletin der Königlichen Akademie der Wissenschaften:" München, Januar, 1853. (From the Akademie.)

"Ueber den Chemismus der Vegetation:" von Dr. A. Vogel, jun. München, 1852.

"Abhandlungen der Mathematisch-Physikalischen Classe der Königlichen Bayerischen Akademie der Wissenschaften:" München, 1853.

"Tafeln zur Vergleichung und Reduction der in verschiedenen Längemaassen abgelesenen Barometerstände:" von J. J. Pohl and J. Schabus.

"Tafeln zur Reduction der in Millimetern abgelesenen Barometerstände auf die Normaltemperatur von 0° Celsius:" Berechnet von J. J. Pohl and J. Schabus.

"Ueber die Anwendung der Pikrinsäure zur Unterscheidung von Geweben vegetabilischen and thierischen Ursprungs:" von Dr. J. J. Pohl.

"Beobachtungen während der Sonnenfinsterniss am 28. Juli 1851:" von J. J. Pohl.

"Nachtrag zur thermo-aräometrischen Bierprobe:" von Dr. J. J. Pohl. Wien, 1852.

"Jahrbuch der kaiserlich-königlichen Geologischen Reichsanstalt für 1851, 1852 and 1853:" Wien.

"Ofversight af Kongl. Vetenskaps Akademiens förhandligar: nionde Årgången 1852, Stockholme, 1853."

A paper was read, entitled:

"Critical Observations on Williamson's Theory of Water, Ethers, and Acids:" by H. Kolbe.

Dr. Williamson offered some observations in reply to this communication.

March 6, 1854.

COLONEL PHILIP YORKE, President, in the Chair.

The following donations were announced:

"The Pharmaceutical Journal for March:" from the Editor.

"The Literary Gazette:" 2 numbers, from the Publishers.

"The Journal of the Society of Arts:" 2 numbers, from the Society of Arts.

"The Journal of the Photographic Society:" 2 numbers, from the Photographic Society.

Frederick Allen, Esq., of Bow Common, was duly elected a Fellow of the Society.

A resolution of the Council, recommending to the Society that the names of seven Members whose subscriptions were greatly in arrear, be removed from the list of Fellows, in accordance with the Bye-laws of the Society, having been read at this and two preceding meetings, was submitted to a ballot and affirmed.

The names removed are: Dr. John Gardener; John Ward,

late of Bishopsgate Street; W. Johnson, late of Birkenhead; J. T. Jullion, late of Old Kent Road; James Mason, late of Holborn; M. Scanlan; P. Henry Smith, late of Parliament Street.

Professor Graham communicated to the Meeting some of the results of his investigations "On the Liquid Condition of Matter."

March 20, 1854.

Colonel Philip Yorke, President, in the Chair.

The following donations were announced:

"The Literary Gazette:" 2 numbers, from the Publishers.

"Journal of the Society of Arts:" 2 numbers, from the Society of Arts.

"Mitchell's Manual of Assaying:" from the Author.

"Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften:" 4 numbers.

"Denkschriften der Kaiserlichen Akademie der Wissenchaften:" Sechester Band.

"Jahrbuch der kaiserlich-königlichen geologischen Reichsanstalt:" No. 2, for April, May and June, 1853, from the Royal Academy of Sciences of Vienna.

"Proceedings of the Royal Society:" from the Royal Society.

George Payne, Esq., and Samuel Highley, Jun., Esq., were admitted Fellows of the Society.

Reginald J. Morley, Esq., and Dr. A Normandy, were duly elected Fellows of the Society.

The following papers were read:

"On Caprylamine:" by William S. Squire.

"On the volatile bases produced by destructive distillation of the Bituminous Shale of Dorsetshire:" by C. Greville Williams.

NOTICES

OF

PAPERS CONTAINED IN OTHER JOURNALS.

By Henry Watts, B.A., F.C.S.

On a New Saline Compound of Cobalt.*

By E. St. Evre.

This compound is formed by the action of an alkaline nitrite on a solution of a proto-salt of cobalt. A solution of nitrite and nitrate of potash (obtained by passing a stream of nitrous gas, resulting from the action of nitric acid on starch, and left to cool) is passed in a fine stream, by means of a pipette, into a cold, concentrated solution of nitrate of cobalt, to which a sufficient quantity of nitric acid has been added to render it strongly acid. Copious red fumes are then evolved, the liquid becomes continually deeper in colour, and at last assumes a very decided red-brown colour. At the same time there is formed a pulverulent substance having a fine yellow tint, which continually increases in quantity as the liquid approaches a state of saturation, and gradually falls to the bottom. As the potash-solution is always alkaline, a blue sub-salt, which always results from the reaction of an alkaline carbonate on a cobalt-salt, is often observed to form as the potash-salt begins to predominate. In that case, it is necessary to add more nitric acid, so as to keep the liquid constantly acid.

The same yellow precipitate is formed when the sulphate or chloride is used; but the nitrate produces it most readily and in greatest quantity. Nitric oxide continues to rise in small bubbles, which rise gently from all parts of the liquid during the whole operation, and its evolution is indispensable to the formation of the precipitate. The operation is stopped when the liquid has become almost colourless; the new substance is then held in suspension, but gradually falls to

* Ann. Ch. Phys. [3] XXXVIII, 177.

the bottom. While the deposition is going on, the liquid must be kept constantly acid; otherwise the precipitate will retain a greenish tinge, arising from the mixture of the blue sub-salt above mentioned with the yellow compound. As soon as the liquid has become clear, it is decanted, and the precipitate several times washed with cold distilled water, till the wash-water becomes neutral to test-paper; after which it is collected on a filter and dried at a temperature between 115° and 120° C.

The new precipitate is nearly insoluble, even in water acidulated with nitric acid; when the solutions used are pure and sufficiently concentrated, an almost complete decoloration of the liquid takes place. The author at first thought that the action of nitrite of potash on a cobalt-salt might furnish the means of effecting a complete separation of nickel and cobalt, inasmuch as nickel, under the same circumstances, does not yield an analogous compound. This expectation, however, was not fulfilled, for the precipitate after all is not absolutely insoluble.

The liquid from which the yellow precipitate has separated contains a small quantity of nitrate of cobalt, which has either remained unacted upon, or has been produced by partial decomposition of the new salt, and a considerable quantity of nitre, which soon crystallizes if the solution be sufficiently concentrated. The action of nitrite of potash on nitrate of cobalt gives rise therefore to the production:—1. of nitric oxide, which escapes and forms red fumes in the air; 2. of nitrate of potash; 3. of the yellow precipitate.

The same yellow precipitate may also be obtained by suspending the blue subnitrate—obtained by precipitating the neutral nitrate with potash—in an excess of the alkaline nitrite, whereupon part of the precipitate is redissolved; the liquid must then be gently agitated, while a thin stream of nitric or hydrochloric acid is suffered to fall into it. This process has the advantage of yielding a larger product in proportion to the quantity of material used; but, on the other hand, the colour of the precipitate is spoiled by a tinge of green, which it retains even after repeated washings with acidulated water.

Lastly, this yellow compound may be formed synthetically by bringing protoxide of cobalt in contact with potash and hyponitric acid, or, which comes to the same thing, a mixture of nitric oxide and oxygen. A rather strong solution of nitrate of cobalt—which need not, however, be pure—is mixed with a sufficient quantity of potash to determine the precipitation of the blue sub-salt, and then, by agitation, that of the rose-coloured hydrated protoxide: the magma thus produced is poured into a wide and tall foot-glass, care being taken to moisten the sides with the liquid, and a stream of nitric oxide passed into it. In a few minutes—as soon indeed as a sufficient quantity of hyponitric acid has been formed—the yellow colour makes its appearance on the

sides of the vessel, and by continuing the passage of the gas, a complete transformation is obtained. The action is sufficiently prompt and decided to be exhibited as a lecture experiment.

This substance possesses the following properties. Its colour is a brilliant yellow. When examined by the microscope, it is found to consist of quadrilateral prisms terminated with triangular facets. It is heavier than water, neutral to litmus, very sparingly soluble in water, perfectly insoluble in alcohol and ether. Sulphide of carbon dissolves traces of it. Water at 100° decomposes it after some time, with separation of nitric oxide, which, by contact of air, is finally converted into nitric acid, part of which is carried off with the vapour of water, and part enters into the composition of the new product; the liquid at the same time acquires a rose colour.

The yellow compound suspended in water, resists the action of a stream of chlorine gas, even if continued for a day. To effect the decomposition and obtain the characteristic rose colour of the ordinary salts of cobalt, the liquid must be heated; red fumes are then evolved, and there remains a double chloride of cobalt and potassium.

The yellow compound under the same circumstances resists equally well the action of a stream of sulphuretted hydrogen, the formation of sulphide of cobalt not beginning till after a considerable time; but sulphide of ammonium blackens it almost instantly.

Acids decompose it, with evolution of red fumes of hyponitric acid.

An aqueous solution of ammonia does not act upon it till after a considerable time, and even then but partially.

Heated by a spirit-lamp in a stream of hydrogen, it gives off vapour of water mixed with abundance of ammoniacal vapours; the same result is, however, obtained under similar circumstances with ordinary nitrate of cobalt. This reaction would indicate the degree of oxidation of the cobalt, if the nitrogen were completely removed by it; but this is not the case. The residue, which has a metallic appearance, still gives off red vapours when treated with sulphuric acid; moreover, the potash which enters into the composition of the salt, melts and forms a kind of varnish over it, which prevents the further action of the gas.

An aqueous solution of potash decomposes the salt, throwing down the hydrated sesquioxide of cobalt. This hydrate gradually loses its water at 100°, retaining only a single equivalent, which it does not give up till heated above 155°. It is moreover slightly soluble in warm water.

The compound heated with sodium in a bent tube is decomposed with violence, leaving a metallic sponge of finely-divided cobalt, which readily acquires metallic lustre by friction.

The salt heated with solid potash or soda in a closed tube does not give off ammoniacal vapours.

When calcined in contact with the air in a tube closed at the bottom, it changes colour and assumes an orange-red tint. At the same time it fuses and gives off small gas-bubbles from the whole of its mass; a very small quantity of water likewise separates from it, and red vapours of hyponitric acid are evolved, together with white vapours of nitric acid. The liquid which distils off has a slight yellow tint, and is so strongly acid that it quickly corrodes the corks. The residue consists of sesquioxide of cobalt and nitrite of potash. If the decomposition be stopped at the moment when the water and the acid-vapours cease to escape, the substance is found to have lost 28·95 per cent of its weight—a loss which corresponds to 2 equivs. of nitrogen, 9 equivs. of oxygen, and 1 equiv. of water. But the products vary with the manner in which the heat is applied and the operation conducted. When the decomposition takes place in an atmosphere of dry nitrogen or carbonic acid, similar results are obtained, excepting that nitric oxide is found among the products, and the red vapours disappear almost as soon as they are formed, being replaced by those of nitric acid. The residue in this case also consists of nitrite of potash and sesquioxide of cobalt. Lastly, when the substance is decomposed by the heat of a charcoal fire, and in a current of carbonic acid, a gaseous mixture is obtained, which, after the carbonic acid has been absorbed by potash, and the nitric oxide by protosulphate of iron, yields pure nitrogen.

The cobalt was estimated by boiling the salt with acetate of soda, mixed with a little acetic acid to neutralize the alkalinity; adding to the dark brown liquid thus obtained an aqueous solution of sulphuretted hydrogen; dissolving the sulphide of cobalt in very dilute nitric acid (a stronger acid would oxidize the sulphur), and at a temperature not exceeding 50° C.; calcining the resulting nitrate to convert it into sesquioxide, and reducing this oxide to the metallic state in a current of hydrogen gas. The sesquioxide must be carefully examined for sulphur, and that substance estimated, if present, and its weight deducted; and the bulb containing the reduced metal must be strongly heated by the blow-pipe; otherwise the metal, which is pyrophoric, will be reoxidized as soon as it comes in contact with the air.

The potash was precipitated by chloride of platinum after the separation of the cobalt. If the cobalt be not first separated, a portion of it is always carried down with the chloride of platinum and potassium. Hydrofluosilicic acid cannot be used to precipitate the potash, because it forms a soluble double hydrofluosilicate of potash and cobalt.—The nitrogen is easily estimated by the usual method.

The following are the results:

		Calculated.	Found.
2N	28	15·73	15·31 to 15·52
8O	64	35·97	36·38 „ 37·27
CbO	38	21·34	20·03 „ 21·01
KO	48	26·96	25·97 „ 26·94
N_2O_8. CbO, KO	178	100·00	

The analytical numbers exhibit a slight deficiency, in consequence of the salt not being quite anhydrous.

With respect to the arrangement of the elements in this compound, we may conclude, from the synthetical mode of preparing it already described (p. 84), that the cobalt is in the state of protoxide. The nitrogen appears to be in the form of nitric and nitrous acid, and we might at first suppose that the yellow salt is a compound of nitrate of potash with nitrite of cobalt, or *vice versâ*. But if that were the case, the salt ought to be formed by the first process (p. 83), without evolution of gas or formation of nitre. Now nitrite of potash is always alkaline, and when treated with acids gives off nitric oxide; and this nitric oxide decomposes the nitric acid present, converting it into hyponitric acid:

$$NO_2 + 2\,NO_5 = 3\,NO_4.$$

Hence the action may be represented by the following equation:

$$CbO, NO_5 + 2\,NO_5 + 4\,(KO, NO_3) = 3\,(KO, NO_5) + 2\,NO_2 + \underbrace{CbO, KO, 2\,NO_4}_{\text{Yellow salt.}}.$$

The formula must however be doubled, first on account of the presence of water in the salt (1 equiv. of water to 2 equivs. of salt), and secondly, because the salt, when decomposed, either by potash in solution or by calcination in contact with the air, yields sesquioxide of cobalt. The formula is therefore as follows:

$$2\,(N_2O_8, CbO, KO), HO.$$

This formula requires:

		Calculation.	Mean of Experiments.
4 N	56	15·34	15·42
16 O	128	35·07	—
2 CbO	76	20·82	—
2 KO	96	26·30	20·48
HO	9	2·47	26·50
	365	100·00	

The salt appears then to be a compound of nitric and nitrous acid with potash, water, and protoxide of cobalt. The exact mode of grouping of the elements cannot at present be determined.

The salt calcined in contact with the air, gives off all its water, and is converted into anhydrous sesquioxide of cobalt, $Cb_3\,O_3$.

This compound, from the beauty of its colour, its permanence, and its capability of resisting the ordinary agents of sulphuration and oxidation, appears to be well adapted for painting. Experiments have been made with it, both as an oil and as a water-colour, alone and mixed with white-lead, mineral blue, and vermilion, and all have yielded satisfactory results. The mixture with vermilion was the only one which underwent any change of colour, assuming a greyish tint; but this is always the case with vermillion when exposed to light. The new pigment may be designated by the name of *Cobalt-yellow.*

On the Decomposition of the Cyanic Ethers.*

By A. Wurtz.

When cyanic ether is placed in contact with water, carbonic acid is disengaged, and diethylurea is formed. On the other hand, this ether acts, with few exceptions, on all the compounds derived from the type water, and the products of the reaction are, to a certain extent, similar to those just mentioned. In fact, carbonic acid is often evolved, and a product is also formed analogous to the *amides.* It is true that diethylurea is not an amide, but it bears a very close relation to that class of bodies; for it is isomeric with diethylo-carbamide, and nothing prevents us from supposing that at the moment of its formation it is produced by the molecular transposition of carbamide. The following formulæ exhibit the existing relations between these products:

$$\underbrace{C_2\,O_2,\,N_2\,H_4}_{\text{Carbamide.}} = \underbrace{N_2\left\{\begin{matrix}H_4\\C_2\,O_2\end{matrix}\right.}_{\text{Urea.}}$$

$$C_2\,O_2,\,N_2\left\{\begin{matrix}H_2\\(C_4\,H_5)_2\end{matrix}\right. = N_2\left\{\begin{matrix}H_2\\(C_4\,H_5)_2\\C_2\,O_2\end{matrix}\right.$$

If then the action of water on cyanic ether gives rise to urea, whereas amides are formed by the action of the derivatives of water on cyanic ether, the relations which exist between these products, and

* Compt. Rend. XXXVII, 180.

consequently the observed analogy between the reactions themselves, are sufficiently established by the preceding considerations. This will be further seen from the following experiments, which, moreover, point out a new mode of formation of the amides.

When cyanic ether is mixed with monohydrated acetic acid, $\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}O_2$, carbonic acid is evolved, and *Ethylacetamide* is produced. The reaction is expressed by the following formula:

$$\underbrace{\left.\begin{matrix}C_4H_3O_2\\H\end{matrix}\right\}O_2}_{\text{Acetic acid.}}+\underbrace{C_6H_5NO_2}_{\text{Cyanic ether.}}=2\,CO_2+\underbrace{N\left\{\begin{matrix}C_4H_5\\C_4H_3O_2\\H\end{matrix}\right.}_{\text{Ethylacetamide.}}$$

This compound was first obtained by M. Wurtz two years ago by the action of ethylamine on acetic ether.

Cyanic ether acts upon anhydrous acetic acid. When these liquids, in about equal volumes, are enclosed in a tube of green glass, the tube hermetically sealed, and then immersed in an oil-bath heated to 180°, the reaction takes place, the products being carbonic acid and ethylo-diacetamide, $N_2\left\{\begin{matrix}C_4H_5\\C_4H_3O_2\\C_4H_3O_2\end{matrix}\right.$, as shown by the following equation:

$$\underbrace{\left.\begin{matrix}C_4H_3O_2\\C_4H_3O_2\end{matrix}\right\}O_2}_{\text{Anhydrous acetic acid.}}+\underbrace{C_6H_5NO_2}_{\text{Cyanic ether.}}=\underbrace{N_2\left\{\begin{matrix}C_4H_5\\C_4H_3O_2\\C_4H_3O_2\end{matrix}\right.}_{\text{Ethylo-diacetamide.}}+2\,CO_2$$

Ethylacetamide and ethylo-diacetamide are evidently analogous to the compound amides* which Gerhardt has obtained by a totally different process. It will readily be understood that the process just described may, like Gerhardt's, be applied to the formation of a large number of new amides.

Alcohol itself may be referred to the type of water. Cyanic ether decomposes it like the preceding compounds, only it does not evolve carbonic acid in this reaction; but the elements of the two bodies combine and group themselves in such a manner as to form ethylurethane. The reaction is as follows:

$$\underbrace{\left.\begin{matrix}C_4H_5\\H\end{matrix}\right\}O_2}_{\text{Alcohol.}}+\underbrace{C_6H_5NO_2}_{\text{Cyanic ether.}}=\underbrace{C_{10}H_{11}NO_4}_{\text{Ethylurethane.}}$$

* Chem. Soc. Qu. J. VI, 193.

Ethylurethane may be regarded as ethylocarbamic ether, and is therefore related to the amides like carbamic acid itself.

Common ether $\left.\begin{matrix}C_4H_5\\C_4H_5\end{matrix}\right\}O_2$ does not act at all, or acts with great difficulty, on cyanic ether. The author enclosed these two highly volatile liquids in very strong tubes, and heated them to very high temperatures at enormous pressures. On opening them after cooling, no evolution of gas was observed; and on distilling the contents, the distillate was found to consist of unaltered ether and cyanate of ethyl. At the end of the distillation, however, at a temperature of 200°, a peculiar volatile liquid passed over, but in quantity too small for analysis. This liquid might be diethylurethane; but from the qualitative examination which the author made of it, this view of its nature appears to be doubtful.

On Selenide of Ethyl or Selenethyl.

By C. A. Joy.*

Selenide of ethyl was discovered in 1836 by Löwig, who obtained it by distilling dry selenide of potassium with oxalic ether. The following experiments, which were undertaken with the view of ascertaining whether this body acts as an organic radical analogous to telluride of ethyl, were made with a product obtained by distilling a solution of selenide of potassium with sulphovinate of potash.

To prepare the monoselenide of potassium, hydrate of potash was dissolved in four parts of water, the solution divided into two equal parts, one portion completely saturated with seleniuretted hydrogen gas, and then the other half added. The seleniuretted hydrogen was evolved by the action of hydrochloric acid on selenide of iron (obtained by heating a mixture of equal parts of iron and selenium in a glass retort). As the gas decomposes in contact with the air, it is necessary to pass a stream of hydrogen through the apparatus before the action begins; the hydrogen-apparatus may also be left in connection while the evolution of the seleniuretted hydrogen is going on, so that at the end of the process hydrogen may be again passed through the apparatus, to drive the last portions of seleniuretted hydrogen into the potash-ley, which should likewise be surrounded by an atmosphere of hydrogen.

The solution of selenide of potassium thus obtained was mixed

* Ann. Ch. Pharm. LXXXVI, 35.

with a concentrated solution of sulphovinate of potash in a flask provided with a condensing tube, and rapidly distilled, the operation being continued as long as drops of selenide of ethyl passed over with the water. For one part of selenium, there were used two parts of hydrate of potash and four pints of sulphovinate.

Selenethyl is a clear, pale, yellow liquid, having a most insufferable odour. It is much heavier than water, and does not mix with it. When set on fire, it burns with emission of red vapours of selenium.

Nitrate of Selenethyl.—Formed by dissolving selenethyl in hot moderately strong nitric acid, the action being attended with evolution of nitric oxide gas. It was not obtained in the dry state, but only in the form of a concentrated solution, which began to decompose when further evaporated. That it really is the nitrate of selenethyl appears from the following experiments:—

Chloride of Selenethyl. C_4H_5SeCl.—The solution of selenide of ethyl in nitric acid behaves with hydrochloric acid just like that of tellurethyl; on the addition of the acid, it becomes milk-white, and immediately afterwards drops of an oily body separate out.

This substance is the chloride of selenethyl. It is a transparent light yellow liquid which sinks in water; when quite pure, it appears to be inodorous. It is somewhat soluble in water, and still more in hydrochloric acid, which circumstance renders some care necessary in preparing it. It was found, by analysis, to contain 33·87 per cent. of chlorine. The preceding formula requires 34·9 per cent.

The greater part of the chloride of selenethyl obtained as above having been left, for a considerable time, in contact with the liquid containing hydrochloric and nitric acid, in which it had been produced, a number of transparent and colourless crystals were observed to form at the separating surface of the two liquids. These crystals were very well defined, and, considering the small quantity, of considerable magnitude. The author was not able to determine the exact nature of this body; but by its mode of decomposition when heated, and its ultimate analysis, it appeared to be an organic compound containing chlorine and selenium. It did not exhibit the characters of a hydrate of the chloride of selenethyl by solution in water, or by any other means. It dissolves readily in water and in alcohols, and separates out unchanged on evaporating the liquids. Its aqueous solution is not clouded by hydrochloric acid; it has an acid reaction. The body appears to be an acid, for it forms, with ammonia, a highly crystalline mass, from which the ammonia is eliminated by potash. Hydrochloric acid did not precipitate chloride of selenethyl from it, a proof that no oxychloride of selenethyl had been formed by the action of the ammonia. On the other hand, sulphurous acid added to it, separated selenethyl. Analysis showed that it contains 13·68

per cent. carbon, 4·298 hydrogen, and 20·05 chlorine; whence we may infer that it contains 4 eq. chlorine to 4 eq. carbon.

Oxychloride of Selenethyl. $C_4H_5SeO + C_4H_5SeCl$.—Chloride of selenethyl dissolves readily in ammonia, producing chloride of ammonium and oxychloride of selenethyl. After evaporating the solution, the oxychloride may be extracted by absolute alcohol. It crystallizes in highly lustrous, colourless cubes, generally grouped in stellate masses. Hydrochloric acid added to its aqueous solution throws down the oily chloride of selenethyl; and sulphurous acid throws down a stinking mixture of selenethyl and the chloride. These reactions indicate its composition.

Bromide of Selenethyl separates in the form of a lemon-yellow oil, sinking in water, when a solution of the nitrate is mixed with hydrobromic acid.

Iodide of Selenethyl. C_4H_5SeI.—Produced when a solution of the nitrate, or even of the chloride, is mixed with hydriodic acid. Black liquid, with a semi-metallic lustre, sinking in water; very much like bromine. It is inodorous, and does not solidify at 0°C.

These two compounds dissolve easily in ammonia, and form an oxybromide and oxyiodide of selenethyl, which, however, have not been further examined.

On the formation of Amarine, Furfurine, and a new Base, Anisine.*

By C. Bertagnini.

Having found that trinitro-hydrobenzamide may be transformed into trinitro-amarine by the mere action of heat, the author was induced to express a hope† that other hydramides might also, by this simple agent, be converted into isomeric bases. Experiments made with this view on hydrobenzamide, furfuramide, and anishydramide have led to satisfactory results.

Pure hydrobenzamide heated for three or four hours to a temperature of 120° to 130° C., yields on cooling a vitreous mass, consisting entirely of amarine. On dissolving this mass in boiling alcohol, and adding an excess of hydrochloric acid, white crystals of hydrochlorate of amarine soon form in the liquid. By one

* Ann. Ch. Pharm. LXXXVIII, 127.
† Ibid. LXXIX, 278.

recrystallization, the salt may be obtained in a state of perfect purity, and very pure amarine may be prepared from it.

The analysis of the salt led to the formula:

$$C_{42}\,H_{18}\,N_2\,.\,H\,Cl.$$

Furfuramide may, in a similar manner, be converted into furfurine, by exposure for half an hour to a temperature of 110° to 120°. By dissolving the resulting brown mass in alcohol, and adding an excess of oxalic acid, a salt is obtained, having all the properties of binoxalate of furfurine, and yielding the base when treated in the usual manner. The facility with which furfuramide is converted into furfurine affords a method of preparing this base directly from furfurol. It is only necessary to pass dry ammoniacal gas into furfurol heated to 110° to 120°; the furfurol then turns brown, and in the course of half an hour or an hour is completely converted into furfurine.

Pure anishydramide, heated in an oil-bath to about 120°, melts into a yellowish liquid, which, if heated for two hours to a temperature of 165° to 170°, is completely converted, without alteration of external appearance, into a new base, isomeric with anishydramide, which may be called *Anisine*. To obtain this base in a state of purity, the product must be dissolved in boiling alcohol, and hydrochloric acid added. The liquid then solidifies, on cooling, to a mass of interlaced crystals, which, when freed from the mother-liquor and decomposed by potash or ammonia, yield the new base in the free state.

Anisine crystallizes in transparent prisms, which are scarcely soluble in water, but dissolve in alcohol and sparingly in ether. The solutions of this base have a strong alkaline reaction and a bitter taste. Its formula is:

$$C_{48}\,H_{24}\,N_2\,O_6.$$

With acids it yields crystallized salts of definite constitution.

Hydrochlorate of anisine crystallizes in white strongly lustrous needles, which dissolve sparingly in water, but readily in alcohol. Dried at ordinary temperatures, it contains $C_{48}\,H_{24}\,N_2O_6.\,H\,Cl + 2\tfrac{1}{2}\,H\,O$; at 100°, it parts with its water, and is reduced to $C_{48}\,H_{24}\,N_2\,O_6\,.\,H\,Cl$.

The platinum double salt forms shining laminæ of a pale orange colour. It dissolves sparingly in alcohol, and is composed of $C_{48}\,H_{24}\,N_2\,O_6\,.\,H\,Cl + Pt\,Cl_2$.

THE

QUARTERLY JOURNAL

OF THE

CHEMICAL SOCIETY.

XI.—*On the Volatile Bases produced by Destructive Distillation of the Bituminous Shale of Dorsetshire.*

By C. Greville Williams.

Among the multitude of remarkable products with which organic chemistry has enriched science, there is, perhaps, no class of compounds which possess more points of interest, and hold out greater hopes of important applications, than the volatile organic bases. Their numerous metamorphoses, very singular constitution, and the many instances of isomerism to be found among them, are quite sufficient to make their history in the highest degree worthy of study, without considering the light which it has been hoped the decompositions attending their examination will throw, on the grand problem of the artificial production of the cinchona alkaloids.

The researches of Anderson, Hofmann, and Stenhouse, have shown it to be more than probable, that all nitrogenous animal and vegetable matters yield volatile organic bases by destructive distillation; and, in the hands of the first-named chemist, bone-oil has been made to yield, not only a number of bases which have, by some, been considered characteristic of the decomposition of the gelatinous tissues, but also several of the alkaloids of the ethyl and methyl series discovered by Wurtz.

Proceeding upon these data, it was easy to foresee that the highly

nitrogenous bituminous shale of Dorsetshire, so rich in semi-fossilised animal remains, would yield organic bases among the products of its destructive distillation, and it became, therefore, a problem of considerable interest, to ascertain their nature and relation to those procurable by analogous processes from recent bones.

Not being in a position to distil the shale itself, and the company's works having been abandoned, the only source of material for experiment became the thick red treacly matter which was produced by agitating the crude naphtha with oil of vitriol, in the process of purification, a quantity of which happened to be at my command.

To separate the tarry matters, the substance referred to was repeatedly boiled with water, which had the effect of resinifying the tar, and enabling it, on cooling, to be removed from the surface.

During the boiling, a large quantity of Runge's pyrrol was evolved, as shown by the extreme rapidity with which slips of fir-wood moistened with hydrochloric acid acquired an intense purplish-red colour when exposed to the steam.

When it was found that no more pitch was formed by boiling, the substance was evaporated to a small bulk, saturated with lime or potash, and distilled; the product was then supersaturated with hydrochloric acid, and the non-basic oil separated; the liquid, on being treated with an alkali and distilled as before, yielded the oily bases, containing a small quantity of ammonia, which was removed by washing with a strong solution of potash, in which they were almost insoluble. After this treatment, the only foreign body present was water, of which they contained about a third of their bulk, and which was separated by sticks of potash.

The entire absence of non-basic oils in the liquid thus procured was proved by its ready and complete solubility in hydrochloric acid; and that the ammonia was perfectly removed, was evident from the ease with which their chlorides dissolved in absolute alcohol. In fact, the temperature at which they were rectified will be shown further on to be too high for ammonia to remain in them.

The liquid obtained by this process was placed in a retort with a thermometer in the tubulature; on heat being applied, ebullition commenced at 200° F., but did not become rapid until 260°; the mercury then rose quickly to 300°, at which point it was stationary for a few minutes; it then rose to 318°, between which point and 322° it was again steady for a short time, but soon commenced rising rapidly, and showed no further tendency to a fixed point.

It being, therefore, evident that the fluid under examination was a mixture of several bases of different boiling points, it was resolved to

subject it to a rigid fractionation, the receiver being changed at every ten degrees, and each fraction thus obtained being again submitted to a similar treatment, that portion only being received as a rectified product which came over between the same points in several successive distillations. In this way upwards of a fortnight was expended before products could be obtained with boiling points at all approaching to constancy; and it is worthy of remark, that whereas at first only a very minute fraction could be obtained below 320°, after about half a dozen rectifications, the product below that point was more in quantity than the united bulk of all the rest of the fractions.

The bases thus obtained are limpid, colourless, highly refractive liquids, having a very singular and persistent odour, adhering strongly to the hands and clothes, and being far more pungent and disagreeable in the lower than the upper fractions; moreover, when the vapour of the former is inspired, the peculiar bitter of picoline is perceived. When the smell of the bases has been on the hands or clothes for some time, it becomes like that of soot.

The fractions burn with a brilliant but smoky flame, and they fume strongly on the approach of a rod wetted with hydrochloric acid.

They dissolve readily in acids with considerable elevation of temperature, and form crystallisable deliquescent salts. They all dissolve readily in alcohol and ether; they precipitate nitrate of copper, and in excess redissolve the precipitate, with production of a fine blue colour; but the reaction is less rapid, and the colour less brilliant, than when ammonia is used.

They absorb carbonic acid, though slowly, the lower fractions doing so more energetically than the higher ones; and, in fact, the intensity of their action may in all cases be said to be inversely as the temperature at which they distil.

They may be divided into two groups by the difference in their solubility, those below 320° dissolving easily in water, and those distilling above that temperature being much less soluble, the insolubility increasing rapidly with the rise of boiling point.

All the fractions form double salts with bichloride of platinum; those of the lower fractions crystallise with facility, the higher ones on the contrary with considerable difficulty.

All the products above 330° strike a yellow colour with fir-wood and hydrochloric acid. Those between 360° and 410° give, when treated with solution of bleaching powder, a beautiful green colour, which is due to the presence in small quantity of a base not yet isolated, to which I have given the name of *Vertidine*. At my request Dr. Anderson examined the fraction about that point from Dippel's oil,

but could not ascertain the presence of vertidine; but, on converting the portion coming over about 355° into a nitrate, and boiling with nitric acid until the aniline was completely destroyed, and then distilling with lime, he obtained a base which gave a feeble green tint with bleaching powder, and otherwise agrees in its general properties with vertidine. Whatever the nature of this base may prove to be, it evidently approximates closely in composition to those which distilled about 410°, since the fraction at that point has precisely the composition of lutidine.

It was attempted to isolate that base by repeated fractionation; but after an immense number of distillations, the base which afforded the green reaction was found to be too small in quantity to afford a chance of fixing it within a moderate range of degrees.

The first fraction obtained was between 200° and 210° F.; the quantity was so small that it was impossible to submit it to so complete a rectification as could have been wished; it was therefore saturated with hydrochloric acid, and bichloride of platinum added in excess. The crystals, which soon precipitated, filtered off, well washed with ether, and dried at 212° F., gave, on combustion, the following numbers:—

I. 6·250 gave 5·490 carbonic acid, and 1·520 water.
7·315 „ 2·440 platinum.
II. 8·430 „ 2·830 „

	Experiment. I.	Experiment. II.	Calculation.		
Carbon . .	23·96	—	24·07	C_{12}	72
Hydrogen .	2·70	—	2·67	H_8	8
Nitrogen .	—	—	4·73	N	14
Chlorine .	—	—	35·59	Cl_3	106·5
Platinum .	33·35	33·56	32·94	Pt	98·8
			100·00		299·3

The base, therefore, is picoline, with the theoretical constitution of which the analysis almost exactly agrees. The true boiling point of picoline is 272°; it would, therefore, appear strange to find it in a fraction collected at 210°, if we did not know how greatly boiling points are modified by even a slight admixture of substances which distil at different temperatures; besides which, the history of the boiling points of these bases is full of anomalies: for instance, aniline, which has absolutely the same composition and atomic weight as picoline, boils 88° above that substance, namely at 360°, and it is

singular that the same difference is found between the isomers lutidine and toluidine, the former boiling at 300° and the latter at 388°.

In fact, the volatile organic bases appear to present more remarkable cases of isomerism than any other class of substances: this will immediately be seen by reference to the highly singular and interesting alkaloids discovered by Dr. Hofmann.

The next fraction analysed was that coming over between 270° and 280°; it was converted into platinum salt and crystallised, the first crop only being used. After drying at 212° it was burnt, and gave the following result:—

7·130 gave 6·835 carbonic acid, and 2·03 water.
8·625 „ 2·740 platinum.

This corresponds to:

	Experiment.	Calculation.		
Carbon . .	26·14	26·81	C_{14}	84
Hydrogen .	3·16	3·19	H_{10}	10
Nitrogen .	—	4·49	N	14
Chlorine .	—	34·00	Cl_3	106·5
Platinum .	31·76	31·51	Pt	98·7
		100·00		313·2

Dr. Anderson obtained, as a mean result of his analyses of platinochloride of lutidine from bone-oil,

Carbon . . .	26·35
Hydrogen . .	3·23
Nitrogen . .	—
Chlorine . .	—
Platinum . .	31·50

The numbers given above, therefore, agree pretty closely with the theoretical constitution of this base, which was discovered by Dr. Anderson among the alkaloids of Dippel's oil, and which, it is believed, has not, until the present time, been observed by any other chemist.

The deficiency in the carbon points to an admixture with picoline, which supposition is to some extent confirmed by the slight excess of platinum. To render this result the more certain, the mother-liquor, from which the crystals analysed were deposited, was evaporated and

set aside, when a second crop was formed, which, on careful ignition, gave the following numbers:—

I. 4·715 gave 1·545 platinum.
II. 8·770 „ 2·880 „

I.	II.	Mean.	Theory (picoline).
32·76	32·83	32·79	32·94

We therefore see at once that the fraction between 270° and 280° consisted, even after repeated rectifications, of a mixture of the two bases, the first crop consisting chiefly of lutidine, and the second of picoline. This result, and many others obtained in the course of the investigation, show that the fractional crystallisation of the platinum-salts of these bodies would be a far more accurate means of separation than distillation; in fact, Dr. Anderson states that he was only deterred from adopting this method by the very large quantity of platinum necessary for the purpose. Moreover, it would avoid the great loss which is inevitably incurred in so many distillations, which arises, not only from the impossibility of condensing the whole of the vapour in an apparatus which has to be taken to pieces every few minutes, but also from the fact that the bases are partially decomposed by exposure to a high temperature, a perfectly colourless distillate becoming brown after boiling for some time.

The next fraction which was analysed was that which came over between 300° and 310°: it had a somewhat less pungent and more aromatic odour than the previous products. It was analysed by passing its vapour over oxide of copper, the usual precautions being taken in all the analyses to prevent the oxidation of the nitrogen from rendering the carbon determination inaccurate.

I. 7·035 gave 20·335 carbonic acid, and 5·385 water.
II. 3·810 „ 10·975 „ 2·950 „

	Experiment.			Calculation.		
	I.	II.	Mean.			
Carbon .	78·83	78·55	78·68	78.50	C_{14}	84
Hydrogen	8·50	8·60	8·55	8·41	H_9	9
Nitrogen .	12·68	12·85	12·77	13·09	N	14
	100·00	100·00	100·00	100·00		107

These analyses, therefore, agree almost exactly with the theoretical

composition of lutidine; and, moreover, the base came over at the temperature which has been assigned to lutidine as its boiling point by the discoverer.

With the intention of confirming the result of the analysis, a determination was made of the platinum in the double salt of that metal, with the following result:—

I. 6·615 gave 2·085 platinum.
II. 4·965 „ 1·580 „

I.	II.	Mean.	Theory.
31·51	31·82	31·66	31·51

Carmidine.—By passing the vapour of the last fraction (lutidine) over red-hot lime, it is decomposed, with deposition of carbon, the lime becoming black to the centre of the fragments, and what appears to be a new base is formed, to which the above name may be given. Its reactions are, perhaps, more marked than any of the volatile bases of this class yet known. With fir-wood and muriatic acid, a beautiful red tint is produced, and with bleaching powder a fine bluish-green, of a different tint and developed in a different manner from that obtained with the same reagent from vertidine, the new base which has been alluded to previously, the colour commencing from the top of the liquid, whereas in vertidine it begins from the bottom. The tint is moreover much less fugitive than that of the other base. Several attempts were made to isolate it, but the very small quantity at my disposal was exhausted before the experiments were sufficiently advanced to enable me to procure it in a state fit for analysis. Unfortunately the platinum-salt as at present procured does not crystallise, but forms a mass of the consistence of Venice turpentine, exceedingly soluble in water and spirit, from a solution in which it is precipitated by ether in the state of oily drops. Results have been obtained which indicate that the mercury-salt will afford the means of ascertaining its constitution. It is possible that the reactions of carmidine may arise from the conversion of a portion of the lutidine into pyrrol and vertidine; and the difference in the manner in which the green colour is developed, may be caused by the presence of some impurity at present unknown: the subject is now under investigation.

The next fraction examined was that between 350° and 360°.

I. 3·850 gave 11·09 carbonic acid, and 3·00 water,
II. 5·425 „ 15·670 „ 4·44 „

	I.	II.	Mean.	Theory.
Carbon . .	78·54	78·77	78·65	78·50
Hydrogen .	8·64	9·09	8·86	8·41
Nitrogen . .	12·82	12·15	12·49	13·09
	100·00	100·00	100·00	100·00

being the same result as the last analysis. The sp. gr. of this fraction was ·928.

The next distillate analysed after this came over between 380° and 440°, the rise of the thermometer being too rapid to allow of intermediate fractions being obtained.

5·255 gave 15·175 carbonic acid, and 4·22 water,

Carbon	78·75
Hydrogen	8·92
Nitrogen	12·34
	100·00

the per-centage composition of lutidine being still indicated,—with, however, a sufficient rise in the carbon and hydrogen to show an admixture of the next base. It is submitted that these last results are important, as showing how greatly the boiling points of this class of bodies are influenced by the presence of bases of closely approximating constitution, but which distil at a higher temperature. It has been shown by Anderson, in his investigation of the Dippel's oil bases, that fractions obtained at considerable thermometric intervals may have almost exactly the same composition, under the circumstances just indicated. In his analysis of the same base, he made use of fractions from 310° to 324°, and in the platinum-salts from 295° to 335°.

There is no doubt, however, that if sufficient material had been at my disposal, so as to allow of a more perfect separation by fractional distillation, the base of the composition found in the last four fractions might have been brought much closer to its real boiling point, and not have extended over so very large a range of degrees as from 300° to 440°. After the distillations had been repeated a great number of times, the chief bulk was condensed into a few degrees on each side of 310°; the fractions, therefore, after 340°, were exceedingly small in quantity, which rendered their further purification by this method impracticable.

The next fraction analysed was that coming over between 440° and 460°.

4·655 gave 13·543 carbonic acid, and 3·825 water,

	Experiment.	Calculation.		
Carbon	79 34	79·33	C_{16}	96
Hydrogen . . .	9·12	9·09	H_{11}	11
Nitrogen	11·55	11·58	N	14
	100·00	100·00		121

being exactly the composition of the base of the picoline series next to lutidine, the discovery of which in bone-oil was communicated to me by Dr. Anderson about a fortnight previous to its being found among the products of the distillation of the Dorsetshire shale. It is believed that no account of it has yet been published. The boiling point was found by Anderson to be about 355°: this discrepancy is easily accounted for, the quantity at my disposal being too small to allow of its being separated perfectly from the next base, which has probably a boiling point of 500°, a small quantity of liquid remaining in the retort at that temperature.

The next fraction that was obtained in sufficient quantity for analysis, came over between 460° and 490°.

3·380 gave 9·845 carbonic acid, and 2·70 water.

Carbon	79·43
Hydrogen	8·87
Nitrogen	11·70
	100·00

This result is too close to the last to allow of our deriving a different formula from it; but there is still another fraction which does not volatilise when the thermometer has risen to 500°, though in too minute a quantity for an accurate examination;* as, however, it was not probable that I should have an opportunity, for a long time, of obtaining the material for another investigation, I was most desirous of pushing the inquiry as far as possible, in the endeavour to demonstrate the presence of the next base of the series, which would be isomeric with cumidine. The first experiment showed me that I was not to expect rigorously accurate results, for that a partial decomposition had taken place was evident from the fact, that, although the substance when first prepared, about two months previously, did

* Somewhat less than a drachm was obtained.

not contain a trace of water, nevertheless, on redistillation, the first portion contained a little of that substance.

The quantity being insufficient for purification, it was introduced into a very small retort, blown on a piece of tube, and brought over very slowly, the product being received in four portions containing about ten drops in each. The first fraction was rejected, as it contained the chief part of the water: the other three were burnt, with the following results :—

I. 3·795 gave 11·277 carbonic acid, and 3·148 water.
II. 4·942 „ 14·540 „ 3·957 „
III. 4·622 „ 13·702 „ 3·445 „

	I.	II.	III.	Mean.		Theory.
Carbon . .	81·04	80·23	80·85	80·70	C_{18}	80·00
Hydrogen .	9·21	8·89	8·28	8·79	H_{13}	9·62
Nitrogen .	9·75	10·88	10·87	10·51	N	10·38
	100·00	100·00	100·00	100·00		100·00

The decomposition which had taken place having acted by removing the hydrogen in the form of water, and also by eliminating some substance or substances containing excess of carbon, as shown by the dark colour of the distillate, renders the very considerable difference between the theoretical and experimental numbers easy of explanation; in fact, it is remarkable that the difference is not greater, especially when it is considered that the circumstances detailed rendered further purification impossible.

Some peculiarities in the character of this base having rendered its history worthy of some examination, I have promised myself to return to the subject as soon as I have obtained a further supply of material; in the meantime I propose to assign it the name of *Parvoline*, in allusion to its small volatility as compared with its associated bases.

If the analyses just given were the only proofs obtainable, I should be diffident in quoting them as decisive evidence of the presence of a new base; but taken in conjunction with the other phenomena observed in the course of the investigation, and especially with the fact of the steady increase in the carbon and hydrogen in the previous fractions, it is submitted that there can be no doubt whatever of the existence in shale naphtha of the isomer of cumidine, in which case we have five members of a group of the general formula $(C_n H_{n-5}) N$, of which the following terms are known :—

Pyridine	$C_{10} H_5 N$.
Picoline	$C_{12} H_7 N$.
Lutidine	$C_{14} H_9 N$.
Anderson's new base . .	$C_{16} H_{11} N$.
Parvoline	$C_{18} H_{13} N$.

It will be seen that the carbon and hydrogen advance by steps of $C_2 H_2$, and that the carbon is always 5 equivalents more than the hydrogen.

It is hoped that this fact, and an examination of their products of decomposition, will soon enlighten us as to their constitution. In a communication recently received from Dr. Anderson, he states that he has discovered picoline to be a nitryle base, which becomes the more remarkable when we consider that the members of this class contain three radicals; and there being in this instance only seven equivalents of hydrogen to divide between the three, their constitution must be extremely singular. This is still more evident in the case of pyridine, where five equivalents of hydrogen have to be divided into three groups. We may probably expect from the labours of Dr. Anderson, with which he is at present engaged, a complete history of the properties and constitution of these remarkable bodies.

It is highly interesting to observe the strict parallelism which exists between the two groups of bases, of which aniline forms the first term in the one case, and pyridine in the other. For example—

Unknown .	$C_{10} H_5 N$.	Pyridine .	$C_{10} H_5 N$.
Aniline . .	$C_{12} H_7 N$.	Picoline .	$C_{12} H_7 N$.
Toluidine .	$C_{14} H_9 N$.	Lutidine .	$C_{14} H_9 N$.
Xylidine* .	$C_{16} H_{11} N$.	New base .	$C_{16} H_{11} N$.
Cumidine .	$C_{18} H_{13} N$.	Parvoline .	$C_{18} H_{13} N$.

One of the aniline series is seen to be wanting—namely, the isomer of pyridine; this term might doubtless be supplied by treating its corresponding hydrocarbon in the same way that aniline is obtained from benzole, cumidine from cumole, &c.†

It is somewhat singular that while aniline is at present the type

* Comptes Rendus, Vol. xxx. p. 319.

† While on this track, I subjected the more volatile portion of coal-tar naphtha to a careful fractionation, and obtained a very small quantity of a product boiling at 110°, which was acted on by nitric acid; but the compound dissolved almost entirely in the large quantity of water into which it was thrown, with the intention of precipitating it, and from which I was unable to separate it in a state fit for the action of sulphuretted hydrogen: this, however, is not a serious difficulty, and I hope very soon to obtain a more satisfactory result.

of the one series, that it is nevertheless found among the bases of Dippel's oil associated with the picoline group, and yet that the latter class, as obtained from the shale products, does not contain a trace of aniline. Stenhouse also demonstrated its absence from the bases obtained by him from beans. It is evident, also, that the last-named chemist's bases have many points of resemblance to those from bones and the Dorsetshire shale: in fact, the formula which he deduces from the analyses of the fraction between 302° and 311° only differs from the constitution of pyridine by 1 equivalent of hydrogen, and the carbon in the portion distilling between 392° and 410° is almost exactly the theoretical amount in that base. The hydrogen, on the other hand, approaches closely to the per-centage in lutidine.

In a specimen of the base from beans, which I was shown by Dr. Stenhouse, I observed the peculiar bitter sensation, on inhaling its vapour, which has been previously alluded to as characteristic of picoline: it becomes, therefore, extremely probable that the bean bases are mixtures of those found in the Dippel's oil and shale products, with some substance easily decomposed and resinified by nitric acid.

It results, in effect, from the experiments detailed, that the bituminous shale yields by its distillation several bases, which are identical with those procured by the same processes both from coal and also from recent bones; but, although this is the case, we cannot but be surprised at the absence of aniline, which, from its marked reactions, had become to a certain extent characteristic of this class of decomposition.

In conclusion, it is suggested that, as in the present state of our knowledge, pyridine forms the first step of the one class, it would be more regular to give its name to the group, instead of calling it the "Picoline Series," as is usually done.

XII.—*On Caprylamine.*

By William S. Squire.

The remarkable alcohol discovered by M. Bouis, in the reaction of hydrate of potash upon castor oil, has been repeatedly analysed by himself and other chemists; the results obtained have been translated into the formulæ $C_{16}H_{18}O_2$, and $C_{14}H_{16}O_2$, whence it is evident that the new alcohol must be either caprylic or œnanthylic alcohol. The

opinions of chemists remaining undecided upon this point, I was induced by Dr. Hofmann to study the ammonias corresponding to this alcohol. The analyses of these compounds, and especially of the higher bases, appeared to be particularly calculated to solve this question; since in forming the fourth bases, for instance, we obtain a much greater difference in the carbon and hydrogen equivalents than in the alcohols from which they are derived. Thus:—

Caprylic alcohol . .	$C_{16}\,H_{18}\,O_2$	Œnanthylic alcohol . .	$C_{14}\,H_{16}\,O_2$
Iodide of Tetracapryl-ammonium .	$C_{64}\,H_{68}\,N\,I$	Iodide of Tetrœnanthyl-ammonium .	$C_{56}\,H_{60}\,N\,I$

The castor oil was saponified by means of solution of caustic potash, and the resulting soap was distilled with a portion of caustic potash amounting to about one-third of the weight of the oil; an energetic action ensued, with an abundant evolution of hydrogen gas and an aromatic oil distilled over, mixed with water. This oil, when separated and rectified, boils at the temperature of 179° C. The quantity of alcohol obtained in this way is about one-fifth of the oil originally employed. If the distillation be continued further, various empyreumatic products pass over, which I have not yet examined.

In order to determine the composition of the alcohol, it was considered desirable to form the ammonia-bases of the series: with this object, the alcohol was saturated with an equal weight of iodine, and the solution decolorised by heating it with phosphorus in a water-bath. The oil thus obtained, when washed with water, is the iodide of the alcohol-radical in a state of tolerable purity. When this body is distilled in a retort, it is found to boil at the temperature of 193°; it does not, however, boil without some decomposition, hydriodic acid being copiously evolved, with formation, probably, of hydrocarbons of the series $C_n\,H_n$.

The iodide was then enclosed with alcoholic ammonia in strong soda-water bottles wired down, and exposed to the heat of boiling water: in about two days combination was effected. A portion was also tried with aqueous ammonia, but at the end of fourteen days no effect had been produced.

The bottles were then opened, and the contents distilled off to one-fourth; the residue was evaporated in a water-bath to a small bulk, in order to get rid of any free alcohol or iodide: it was then distilled with potash. The distillate, dehydrated by means of caustic potash, and rectified, was a colourless liquid, of a strong alkaline reaction, bitter taste, and fishy odour, acting on the skin like potash: it boiled at 164°; the sp. gr. was 0·786.

When dissolved in dilute hydrochloric acid, and mixed with

bichloride of platinum, it furnished a platinum-salt of a magnificent golden colour, soluble to a certain extent in cold water, much more so in hot, pretty soluble in alcohol, and very much so in ether. It was purified by crystallisation from hot water, from which it was deposited in large thin plates. It furnished the following results on analysis :—

0·4816 grm.	yielded	0·1414 grm.	of platinum		= 29·36	per cent.	
0·1982 „	„	0·0584 „	„		= 29·46	„	
0·2485 „	„	0·2583 „	of carbonic acid		= 28·35	„	of carbon.
0·1982 „	„	0·2096 „	„	„	= 28·39	„	„

The base itself, when burned with oxide of copper, gave the following results :—

0·2000 grm.	yielded	0·5450 grm.	of carbonic acid	= 74·34	per cent.	of carbon.
„ „	„	0·2650 „	of water	= 14·72	„	of hydrogen.
0·1745 „	„	0·4750 „	of carbonic acid	= 74·24	„	of carbon.
„ „	„	0·2277 „	of water	= 14·49	„	of hydrogen.

If we compare the per-centages obtained, with those calculated from the theoretical formulæ of caprylamine ($C_{16}H_{19}N$), and œnanthylamine ($C_{14}H_{17}N$) we shall see that the results obtained correspond much more closely with that of the former base:

	Mean of Experiments.	Theory. Caprylamine.	Œnanthylamine.
Carbon .	74·29	74·41	73·04
Hydrogen .	14·61	14·72	14·78
Nitrogen .	11·10	10·97	12·18
	100·00	100·00	100·00

PLATINUM-SALT.

	Mean of Experiments.	Theory. Caprylamine.	Œnanthylamine.
Platinum .	29·41	29·5	30·7
Carbon .	28·37	28·6	30·6

These numbers, I think, must lead us to consider the base produced under the above-mentioned circumstances as caprylamine, and to assign to it the formula $C_{16}H_{19}N$, and to its platinum-salt the formula $C_{16}H_{20}N$, $PtCl_2$; and, therefore, to regard the alcohol from which it is derived, as the alcohol of the capryl series, a conclusion at which my friend M. Moschnin* has likewise arrived.

When I shall have completed the investigation of the other bases, and especially of the fourth, I hope to present still further expemental evidence of the view which I have ventured to advance.

* Ann. Pharm. lxxxvii. 1.

XIII.—*Critical Observations on Williamson's Theory of Water, Ethers, and Acids.*

By H. Kolbe.

The hypothesis lately proposed by Williamson* respecting the constitution of water, and of the alcohols, ethers, and acids, has rapidly gained adherents—as shown by the recent highly meritorious labours of Gerhardt, Chancel, and others—and appears to have excited considerable attention in all quarters, inasmuch as it affords a simple and plausible explanation of a large number of phenomena, and seeks to unite the most heterogeneous compounds under one point of view.

The proposer of a new hypothesis is bound to show—first, that the facts on which it is based are either totally inconsistent with established views, or at least less consistent than with his own,—and secondly, that the new hypothesis maintains itself in its consequences. Neither of these points has been attended to by Williamson. Moreover, this hypothesis has hitherto been regarded solely from the particular point of view selected by its adherents. I will endeavour to view it in a different light.

Williamson grounds his theory of the constitution of alcohol and ether—which are expressed by the formulæ,

$$\left.\begin{matrix}C_2\,h_5\\h\end{matrix}\right\}O \text{ (alcohol), and } \left.\begin{matrix}C_2\,h_5\\C_2\,h_5\end{matrix}\right\}O \text{ (ether)—}$$

principally on a new mode of forming ether discovered by himself, viz. from ethylate of potash and iodide of ethyl, considering this reaction in connection with the formation of a new ether (vinomethylic ether), which, according to his hypothesis, contains $\left.\begin{matrix}C_2\,h_5\\C\,h_3\end{matrix}\right\}O$, and is obtained in a similar manner by the action of ethylate of potash on iodide of methyl. These results he regards as affording so incontrovertible a demonstration of the correctness of his view, that he dismisses the idea of explaining the above-mentioned formation of ether by the old theory—according to which, ethylate of potash and iodide of ethyl would be supposed to yield iodide of potassium and 2 atoms of oxide of ethyl—with the simple remark "that the insufficiency of this explanation becomes evident on a little reflection."

* An. Ch. Pharm. [2], i. 37; v. 73; Chem. Soc. Qu. J. iv. 106 and 229.

But the older ether-theory has so long been regarded as a main pillar of theoretical organic chemistry, that it is really entitled to a more systematic refutation than is afforded by this very summary dismissal.

If, as is here done by Williamson, we regard the mode of formation of a body as alone sufficient to determine its chemical constitution, we shall be led in many instances to rather startling conclusions. Williamson's mode of reasoning, applied to the action of sulphuretted hydrogen upon sulphurous acid ($2\,H\,S + S\,O_2 = 2\,H\,O + 3\,S$), might lead to the conclusion that the sulphur-molecule thus set free is composed of 3 atoms of sulphur, or that it is a compound whose formula is $S_2\,S$. Just as Williamson sees a confirmation of his hypothesis respecting the constitution of ether, in the fact that ethylate of potash and iodide of methyl yield, not a mixture of vinic and methylic ethers, but his compound, $\left.\begin{matrix} C_2\,h_5 \\ C\,h_3 \end{matrix}\right\}O$, so might we, from the known reaction of sulphuretted hydrogen and selenious acid—which likewise yields, not a mixture of sulphur and selenium, but sulphide of selenium, $S_2\,Se$—deduce an argument in favour of the above-mentioned hypothesis that the atomic weight of the sulphur set free in this reaction is three times as great as that which is usually attributed to sulphur.

"It is clear," says Williamson, "that if alcohol contains ether and water, and the carburetted hydrogen (ethyl) in the first experiment formed a second atom of ether by taking the place of the hydrogen of this water, the process being the same in the second experiment, we should then have obtained two ethers; whereas, if the formation of ether from alcohol be effected by synthesis, a new carburetted hydrogen being added to the one already contained in the alcohol, we ought to obtain the new intermediate ether which was really produced."

That this body may also be regarded as a compound of vinic ether with methylic ether $= C_4\,H_5\,O, C_2\,H_3\,O$, is an idea which Williamson appears altogether to ignore. Perhaps, however, it is this view of which he says that its inadmissibility becomes evident on a little reflection. I presume, indeed, that Williamson regards the oxides of ethyl and methyl as altogether incapable of uniting into a stable compound, on account of the great similarity of their chemical properties. This prejudice, however, is easily refuted by analogies from inorganic chemistry. Nobody has yet found any difficulty in admitting the existence of chemical compounds of selenium and sulphur, $S_2\,Se$, or of chlorine and iodine, $I\,Cl$ and $I\,Cl_3$, which are, however,

quite as closely allied to each other as the oxides of ethyl and methyl. Why then should the existence of the compound $C_4H_5O.C_2H_3O$ be less admissible?

Similar remarks apply to the compounds which Chancel has obtained by distilling sulphomethylate of potash with carbovinate of potash, and oxalomethylate of potash with sulphovinate of potash,—viz. the double compounds: $C_4H_5O.CO_2 + C_2H_3O.CO_2$ and $C_4H_5O.C_2O_3 + C_2H_3O.C_2O_3$, which may be classed with the many well-known double salts of inorganic chemistry.

I must here, however, expressly observe that the preceding remarks are by no means intended as a complete refutation of Williamson's hypothesis on the constitution of the alcohols and ethers; but I think I can show by facts the untenability of his acid-theory. At present I will merely remark that Williamson, by the facts which he has adduced, has fallen equally short of giving a satisfactory proof either of the correctness of his own views, or the insufficiency of the hitherto received theory of the alcohols and ethers. Neither does his more recent observation—that a mixture of equivalent weights of the hydrated oxides of amyl and ethyl distilled with sulphuric acid, yields the so-called amyl-ethylal—afford any argument in favour either of his own or of any other theory, inasmuch as the old ether-theory affords an equally satisfactory explanation of this formation of the compound $C_{10}H_{11}O.C_4H_5O$.

Williamson has applied his ideas to an apparently very simple explanation of the process of etherification. He supposes, namely, that the alcohol and sulphuric acid first form water and sulphovinic acid, which latter body then acts upon another portion of alcohol in such a manner as to form ether and sulphuric acid, which latter then again gives rise to the production of sulphovinic acid, &c. He represents this process by the following equations:—

$$\underbrace{\left.\begin{matrix}h\\h\end{matrix}\right\}SO_4}_{\text{Sulphuric acid.}} + \underbrace{\left.\begin{matrix}C_2h_5\\h\end{matrix}\right\}O}_{\text{Alcohol.}} = \underbrace{\left.\begin{matrix}C_2h_5\\h\end{matrix}\right\}SO_4}_{\text{Sulphovinic acid.}} + \left.\begin{matrix}h\\h\end{matrix}\right\}O$$

$$\left.\begin{matrix}C_2h_5\\h\end{matrix}\right\}SO_4 + \left.\begin{matrix}C_2h_5\\h\end{matrix}\right\}O = \left.\begin{matrix}C_2h_5\\C_2h_5\end{matrix}\right\}O + \left.\begin{matrix}h\\h\end{matrix}\right\}SO_4$$

The latter equation, translated into the language of the old theory, takes the following form:—

$$C_4H_5O.SO_3 + HO.SO_3 + C_4H_5O.HO = 2C_4H_5O + 2(HO.SO_3)$$

Whatever hypothesis we adopt respecting the formation of ether by sulphuric acid—unless, indeed, we regard contact-action as the cause of it—it still remains inexplicable how sulphovinic acid can be first resolved into ether and sulphuric acid, and then reproduced at the very same temperature. Williamson has endeavoured to remove this difficulty by a new hypothesis, viz. that the constituent atoms of all chemical compounds are in a state of constant motion.

He says, at the end of his first paper: "In using the atomic theory, chemists have added to it of late years an unsafe and perhaps unwarrantable hypothesis: namely, that the atoms are in a state of rest. This hypothesis the author of the present paper discards, and reasons on the broader basis of atomic *motion*."

This categorical declaration may perhaps serve to cut the knot, but will assuredly not untie it. Williamson has taken care to ensure by examples that his meaning shall not be misunderstood.

"We are thus forced," he says, "to admit, that, in an aggregate of molecules of any compound, there is an exchange constantly going on between the elements which are contained in it. For instance, a drop of hydrochloric acid being supposed to be made up of a great number of molecules of the composition Cl H, the proposition at which we have just arrived would lead us to believe that each atom of hydrogen does not remain quietly in juxtaposition with the atom of chlorine with which it first united, but, on the contrary, is constantly changing places with other atoms of hydrogen, or what is the same thing, changing chlorine." Williamson finds a proof of this conception in the well-known fact that sulphate of copper and hydrochloric acid, when mixed, are partly converted into chloride of copper and sulphuric acid.

If, however, this constant interchange of the individual hydrogen and chlorine atoms really takes place in aqueous hydrochloric acid, how much more readily must it go on in hydrochloric acid gas. But unless we suppose that in this gaseous compound, each atom of hydrogen is firmly united to an atom of chlorine, in what respect does a mixture of equal volumes of chlorine and hydrogen differ from hydrochloric acid gas?

Moreover, if this motion of the atoms causes sulphovinic acid and alcohol to interchange the groups of atoms C_2 h_5 and h, how is it that a mixture of these two compounds does not contain free sulphuric acid, or smell of ether, or yield a stratum of ether when mixed with water? According to the preceding hypothesis, we might also expect that a mixture of the alcoholic solutions of chloride of ethyl and

nitrate of silver would yield a precipitate of chloride of silver, which is known not to be the case.

I think I may confine myself to these few objections to Williamson's hypothesis on the motion of the atoms in chemical compounds, stating at the same time my conviction that the author himself will, after fuller consideration, withdraw it.

With regard to the formation of ether from alcohol and chloride of zinc, Williamson remarks how easily it is explained by his ether-theory. Alcohol and chloride of zinc form, according to his view, the so-called zinc-alcohol and hydrochloric acid, which with alcohol again yields chloride of ethyl and water, whereupon the chloride of ethyl and zinc-alcohol act on one another in such a manner as to form ether and chloride of zinc. Even if it be really so,—a point by no means established,—the successive transformations may be explained just as readily by the old ether-theory, as indeed is evident from comparison of the two following sets of equations:—

$$\left.\begin{matrix}C_2\,h_5\\h\end{matrix}\right\}O + zn\,cl = \left.\begin{matrix}C_2\,h_5\\zn\end{matrix}\right\}O + hcl$$

$$\left.\begin{matrix}C_2\,h_5\\h\end{matrix}\right\}O + h\,cl = C_2\,h_5\,.\,cl + \left.\begin{matrix}h\\h\end{matrix}\right\}O$$

$$C_2\,h_5\,.\,cl + \left.\begin{matrix}C_2\,h_5\\zn\end{matrix}\right\}O = \left.\begin{matrix}C_2\,h_5\\C_2\,h_5\end{matrix}\right\}O + zn\,cl$$

$$C_4\,H_5\,O\,.\,H\,O + Zn\,Cl = C_4\,H_5\,O\,.\,Zn\,O + H\,Cl$$

$$C_4\,H_5\,O\,.\,H\,O + H\,Cl = C_4\,H_5\,Cl + 2\,H\,O$$

$$C_4\,H_5\,Cl + C_4\,H_5\,O\,.\,Zn\,O = 2\,C_4\,H_5\,O + Zn\,Cl.$$

Williamson has not stated whether the formation of ether from alcohol and fluoride of silicium can be explained in a similar manner by the above hypothesis.

Science is indebted to every one who illustrates a series of phenomena from a new point of view, and enriches it with new hypotheses; especially when these hypotheses admit of so extensive an application as that proposed by Williamson. For even the less tenable hypotheses confer great benefit on science, through the opposite exertions of their partizans and opponents. But science has likewise a right to demand that, in the promulgation of new ideas, not only those facts

shall be brought forward to which the new views readily adapt themselves, but further, that the points with which they are less accordant shall be distinctly marked. But if this condition can be imposed, when an author brings forward an hypothesis without pretending that it possesses essential advantages over that which has been previously accepted, but merely places it side by side with the other, and leaves the relative merits of the two to be decided by the reader or by subsequent investigations, much more is such caution required on the part of one who states his views with the certainty and pretensions to infallibility, which many modern theorisers (Gerhardt, for example) are in the habit of assuming.

Williamson is likewise open to objection in this respect. I have already stated that he has omitted to notice the weak points of his hypothesis, and to meet the objections which may be raised against it. This remark applies especially to this acid-theory, the defects of which cannot have escaped him, or at all events would not, if he had carefully weighed the consequences to which it leads.

According to Williamson's theory, the hydrated acids are constituted similarly to water and the alcohols. Acetic acid, for example, is water, $\left.\begin{matrix}h\\h\end{matrix}\right\}O$, in which one of the hydrogen atoms is replaced by the oxygen-radical C_2h_3O (to which he gives the name of *othyl*):

Hydrated acetic acid $\left.\begin{matrix}C_2h_3O\\h\end{matrix}\right\}O$

Acetic ether . . . $\left.\begin{matrix}C_2h_3O\\C_2h_5\end{matrix}\right\}O$

Acetate of potash . $\left.\begin{matrix}C_2h_3O\\k\end{matrix}\right\}O$

that is to say, in other words, that in hydrated acetic acid, the members C_2h_3O and h, in acetic ether C_2h_3O and C_2h_5, and in acetate of potash C_2h_3O and K, occupy, relatively to the oxygen, the same position as the two simple hydrogen-atoms in water. Thence, however, it would necessarily follow that hydrated acetic acid, or acetate of potash, should be decomposed by electrolysis in a manner similar to the analogously constituted compound, water. At the negative pole, therefore, at which water, when subjected to galvanic decomposition, evolves hydrogen gas, acetate of potash when similarly treated should yield potassium (*i. e.* oxide of potassium and hydrogen) and othyl, or its hydrogen-compound, *i. e.* aldehyde. Now I showed some time

ago, that in this decomposition, not the slightest trace of a carbon-compound appears at the negative pole,—nothing, in fact, but hydrogen; while at the positive pole, the chief products obtained are methyl-gas and carbonic acid.

That Williamson should have taken no notice of this investigation on the electrolysis of acetate of potash, appears especially remarkable, when we consider that the facts therein established are adapted, above all others, to serve as a touchstone of any new hypothesis respecting the constitution of acetic acid. The single fact that neither othyl nor any of its products of decomposition is set free at the negative pole is, in my opinion, quite sufficient to demonstrate the inadmissibility of Williamson's acid-theory.

The formation of acetic acid from cyanide of methyl, described by Frankland and myself, together with the reproduction of cyanide of methyl from acetate of ammonia by simple abstraction of water, as observed by Dumas, affords the strongest confirmation of the supposition that one-half of the carbon-atoms in acetic acid exists in a mode of combination different from that of the other half,—and deserved, therefore, to be taken into account in the laying down of any hypothesis respecting the constitution of acetic acid. Williamson appears to attach but little importance to these facts, inasmuch as he completely ignores them; whereas they must, I think, if carefully considered, have convinced him that his othyl does not exist in the acetyl-compounds in the form which he assigns to it.

On the facts just stated, and taking into account all the chemical relations of acetic acid with which I am acquainted, I have based the hypothesis that the acetyl-compounds contain the so-called conjugated radical $(C_2 H_3)^{\frown}C_2$; and, although Williamson* regards this hypothesis as too complicated, and replete with unintelligible symbols, I am unable to see, in the many highly important additions which have since been made to the chemical history of acetic acid, anything but a further confirmation of my views.

At the time when this hypothesis was proposed, cacodyl was the only known radical of analogous constitution to the hypothetical acetyl $(C_2 H_3)^{\frown}C_2$; but we have since become acquainted, not only with directly prepared compounds of various metals with the homologues of hydrogen, but also with compounds of selenium and tellurium with ethyl, forming conjugated radicals of like nature. Since, then, we are justified in supposing that the elements in general possess the power of uniting with organic hydrocarbons to form conjugated

* Phil. Mag. [4], vi. 205.

radicals, why, we may ask, should this property be denied to carbon?

Since Gerhardt and Chiozza's recent and highly important researches have proved the correctness of Liebig and Wöhler's original benzoyl-theory, and it can therefore scarcely be doubted that an oxygenised radical occurs in acetic acid and other acetyl-compounds, the old acetyl $(C_2H_3)^{\frown}C_2$ naturally presents itself as the ultimate, and the group $(C_2H_3)^{\frown}C_2O_3$ as the proximate radical of these compounds: the latter may be called *acetoxyl*.

Although I am far from regarding my hypothesis as infallible, still I cannot avoid giving it the preference above all others, especially the easily refuted theory proposed by Williamson, because it gives a natural and satisfactory explanation of *all* the known phenomena to which it has yet been applied, and at the same time is not at all complicated, as Williamson asserts it to be. I am quite prepared to abandon it, as soon as Williamson shall have shown that in any one of its consequences it is as untenable as his own.

Gerhardt, who has adopted Williamson's hypothesis, now also regards the anhydrous organic acids which he has discovered, as water in which both the hydrogen-atoms are replaced by complex groups of atoms containing oxygen. Thus, anhydrous acetic acid $= \left.\begin{matrix}C_2h_3O\\C_2h_3O\end{matrix}\right\}O$; benzo-acetic acid $= \left.\begin{matrix}C_2h_3O\\C_7h_5O\end{matrix}\right\}O$ (a formula which is equivalent to $C_{14}H_5O_3 . C_4H_3O_3$ or $(C_{12}H_5)^{\frown}C_2O_3 . (C_2H_3)^{\frown}C_2O_3$).

If we disregard the arguments which may be deduced from the boiling points and vapour-densities of these and similar compounds in favour of the above theory—arguments which cannot be regarded as convincing till the dependence of boiling points on the mode of combination of the elements of compounds shall be accurately determined, and some proof shall be given that all organic compounds in the gaseous state occupy 2 volumes (at present a mere hypothesis of Gerhardt's) —we shall seek in vain, in the writings of Williamson and Gerhardt, for any arguments adapted to support their acid-theory. They seem, indeed, to regard the apparent simplicity with which their theory unites bodies of the most various kinds under one point of view, as a sufficient proof of its correctness, and appear, for this reason, to have neglected to seek for other arguments in its favour.

It would be extremely interesting to ascertain whether in anhydrous acetic acid—which, according to Gerhardt, is $\left.\begin{matrix}C_2h_3O\\C_2h_3O\end{matrix}\right\}O$—the six

atoms of hydrogen can be replaced, one by one, by chlorine. The existence of an anhydrous acetic acid in which 1, 3, or 5 atoms of hydrogen are replaced by chlorine, would at least show that an atom of this compound contains 6 atoms of hydrogen, and not merely 3, as required by the formula $(C_2\frown H_3)\frown C_2 O_3$. A similar conclusion might be drawn respecting the atomic weight of ether, $\left.\begin{matrix} C_2 h_5 \\ C_2 h_5 \end{matrix}\right\} O$, if experiment should demonstrate the existence of a substitution-product of that body in which 1, 3, 5, 7, or 9 atoms of hydrogen were replaced by chlorine or any other element. The known results of the experiments instituted by Malaguti and Regnault on the action of chlorine upon ether appear, however, to be unfavourable to this idea.

Still more important would it be to ascertain whether anhydrous acetic acid, or other similar bodies, such as ethylate of potash, are conductors of the galvanic current, and, if so, in what manner they are decomposed by it. Since anhydrous acetic acid and ethylate of potash, $\left.\begin{matrix} C_2 h_5 \\ K \end{matrix}\right\} O$, are supposed to be constituted similarly to water, it is reasonable to expect that when they are electrolysed, the carbonated compounds which replace the hydrogen of the water, or, at all events, certain products of their decomposition, will be set free at one pole, and oxygen at the other.*

I will notice one more confutation of Williamson's acid-theory—that, namely, which is derived from the constitution of the salts containing a sesquioxide as their base. How, for instance, can the constitution of benzoate of sesquioxide of iron be reconciled with the assumption that all the salts of benzoic acid are constituted according to the general formula: $\left.\begin{matrix} C_7 h_5 O \\ m \end{matrix}\right\} O$, (m = 1 at. metal)? Gerhardt has foreseen this difficulty, and to save his theory, has resorted to the hypothesis that many metals—iron, aluminum, chromium, &c.—have two or more equivalents. Ferrous chloride, fe cl (Fe=2 fe), has, according to this supposition, a constitution similar to that of ferric chloride, the only difference being that the latter contains another modification of iron, fe β, the equivalent of which is only two-thirds as great as that of the metal contained in ferrous chloride. The similarity of composition of the ferrous and ferric benzoates will then be seen from the following formulæ:—

* Mr. Guthrie is at present engaged in my laboratory with the investigation of this matter, and will shortly publish his results.

Ferrous benzoate . . $\left.\begin{matrix}C_7h_5O\\fe\end{matrix}\right\}O.$

Ferric benzoate . . . $\left.\begin{matrix}C_7h_5O\\fe\beta\end{matrix}\right\}O.$*

These formulæ imply that iron, after being dissolved in hydrochloric acid, is, by the mere passage of chlorine gas into the solution, induced to assume a new equivalent; or, in other words, is converted into a new metal? and that, when this solution is subsequently heated with iron, the original metal is reproduced?

I consider it superfluous to adduce any additional facts against this hypothesis. I will, however, point out one of its consequences, which even a prejudiced investigator cannot but acknowledge as legitimate, viz. that if alum—iron-alum, for example—is really, as Gerhardt supposes,

$$(k_{\frac{1}{2}}\,fe\beta_{\frac{3}{2}})SO_4,\ \text{or}\ \left.\begin{matrix}k\\k\end{matrix}\right\}SO_4+3\left.\begin{matrix}fe\beta\\fe\beta\end{matrix}\right\}SO_4,$$

no reason can be assigned against the possible substitution of $fe\beta$ by fe or k. A double salt, composed of 1 at. sulphate of potash and 3 at. ferrous sulphate, or even $\left.\begin{matrix}k\\k\end{matrix}\right\}SO_4+3\left.\begin{matrix}k\\k\end{matrix}\right\}SO_4$—that is to say, $KO,SO_3+3(KO,SO_3)$—would therefore be an alum; or, in other words, there would exist a sulphate of potash crystallising in octahedrons or in cubes,—that, namely, whose molecule contained four atoms of $KO.SO_3$.

I am under the necessity of adding in this place a few explanatory observations on the tendency of the inquiry which Wrightson† undertook, at my instigation, on the action of an alcoholic solution of potash upon a mixture of cyanide of ethyl and cyanide of amyl, inasmuch as Williamson‡ appears to have misunderstood it; asserting, namely, that Wrightson has used the results of this investigation as arguments against the othyl-theory. Now that investigation was by no means intended to refute Williamson's theory; for Wrightson, when he commenced his experiments, regarded the inaccuracy of that theory as completely proved by the facts above adduced, and by others of like nature. His object was rather—as, in fact, he distinctly stated—to settle the question whether water

* Some passages are omitted which do not appear relevant to Dr. Kolbe's argument.

† Phil. Mag. [4], vi. 88.

‡ Phil. Mag. [4], vi. 204.

might be supposed to contain *two* elementary atoms of hydrogen replaceable by analogous radicals.

From his point of view—he regards acetic acid as the oxide of the conjugated radical $(C_2H_3)^{\frown}C_2$—the question raised by Williamson, as to whether water contains two separately replaceable atoms of hydrogen united with 1 atom of oxygen, possessed a peculiar interest; since, in that case, acetyl must be supposed to contain two atoms of methyl, viz. 2 C h_3, one of which might be replaced by another homologous hydrocarbon. Since now, on this supposition, the formation of acetic acid from cyanide of methyl is due to the reaction of 2 atoms of the latter, viz. of 2 (C h_3, C n), with 3 atoms of water, $3\left.\begin{matrix}h\\h\end{matrix}\right\}O$, it is natural to suppose that a mixture of cyanide of methyl and another analogous cyanic ether, will yield an acetic acid in which one of the atoms of methyl is replaced by another hydrocarbon. Had the experiments instituted by Wrightson for the decision of this question led to a favourable result, an available argument would thereby have been gained for the correctness of Williamson's theory of the constitution of water and of the alcohols (but not of his acid-theory). The contrary result to which those experiments have led is, in the same degree, calculated to weaken our confidence in that hypothesis.

XIV.—*On Dr. Kolbe's Additive Formulæ.*

By Alexander Williamson, Ph.D.

Some time has now elapsed since a paper was published in the Philosophical Magazine under the title "On the Atomic Weight and Constitution of the Alcohols," by F. Wrightson, Ph.D.

The author obtained a mixture of propylic and caproic acids by the action of alcoholic potash on a mixture of cyanide of ethyl and cyanide of amyl,—a result by no means surprising, as those acids are well known to be the products of the decomposition of the respective cyanides. It appears, however, that Dr. Kolbe conceived the possibility of a new intermediate acid being formed in this process; that he thought it must be formed, if certain views which I hold of the constitution of water are correct; and the negative result of the experiments was accordingly cited as an argument against those views. Unfortunately for the author, but more especially for the suggestor of those experiments, the conception was completely erroneous; and had Dr. Kolbe taken the trouble to become acquainted with the recent theory of the constitution of those acids, he would have seen that the imaginary new compound is as inconceivable according to *that*, as it is according to his own theory. The author of the paper seems to have worked under the direction of Dr. Kolbe, and I had occasion to explain to him the nature of his mistake while the paper was yet unpublished in this country. On its subsequent publication, I was induced, by my respect for the important services of Dr. Kolbe, from whom it really emanated, to publish a few words in explanation of the misconception which pervades the paper; showing that the result imagined by Dr. Kolbe was by no means a consequence of the theory to which he attributed it, as it is even less possible according to that, than according to any other theory.

Instead of frankly acknowledging his error, Dr. Kolbe now attempts to justify it by writing the above paper,* professedly dis-

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cussing my views. It thus becomes incumbent on me to offer a few further remarks on the subject; and in analysing his arguments I shall unavoidably be led to explain, more particularly than I had wished to do, the characteristic defects and errors of Dr. Kolbe's theoretical notions to which his original misconception was owing. As the discussion is of Dr. Kolbe's own seeking, he will of course not be offended at my freedom in criticising his views.

Dr. Kolbe says that the experiments on the action of alcoholic potash on the cyanides of ethyl and amyl were not intended to test the correctness of the othyl-theory, as he considered that theory sufficiently disproved before the experiments were begun. All he expected from these experiments was a test of the correctness of the view which represents the hydrogen in water as divisible. If I understand his argument correctly, it is as follows: The compound $(C_2 H_3)\urcorner C_2$ (acetyl) must contain two atoms of methyl, if water contains two atoms of hydrogen, and accordingly one of the two might be replaced by an atom of its homologue, ethyl or amyl, &c. Now, in reasoning thus Dr. Kolbe forgets, singularly enough, that his premises have no acknowledged connexion with the question at issue, and are entirely of his own invention. For the radical $(C_2 H_3)\urcorner C_2$ only exists in the imagination of Dr. Kolbe; and chemists were never before informed that it possesses a constitution analogous to that of water, to such an extent that, if its methyl cannot be halved, the hydrogen of water must be likewise indivisible. The theory which Dr. Kolbe professes to controvert never acknowledged the existence of this radical containing methyl and carbon, but explained the constitution of the acetic acid series in a totally different manner; and it cannot reasonably be blamed for the inaccurate conclusions to which the interpolation of this notion may have led the learned professor and his pupil. I am so convinced of Dr. Kolbe's good faith and sincerity in this peculiar argument, that I must attribute to an entire misconception of the matter on his part, the circumstance of his thus laboriously proving, as subversive of my views, a fact which necessarily follows from them.

But Dr. Kolbe has not only mistaken the general position of the question,—he is equally inaccurate in his descriptions of the individual reactions upon which it turns. He states that cyanide of methyl is decomposed by three atoms of water; thus implying that anhydrous acetic acid is formed in a decomposition which everybody knows is

brought about by the action of hydrate of potash, and in which the alkali is transformed into the acetate, their action being empirically

$$C H_3 C N + \frac{H}{K}{}^{3}O_2 = C_2 H_3 K O_2 + N H_3.$$

Of course Dr. Kolbe did not mean to deny the well-known fact that hydrate of potash is the active agent in this reaction; but his habits of reasoning on chemical reactions are so peculiar that he really thought he had described the process fairly, in obtaining an uneven number of atoms by the omission of the potash, and thus making it appear that the formulæ could not be halved, as they ought to be according to the view which he controverts.

Throughout the whole of his paper, Dr. Kolbe shows himself singularly unacquainted with the views which he endeavours to controvert, and one is really inclined to doubt whether he ever honoured them with any serious consideration before sitting down to write his paper. It is difficult, without such a supposition, to account for the fact that in some of the most important points, the author adopts the new theories, and, in fact, suggests their principles as the most natural explanation of phenomena. Indeed, Dr. Kolbe's paper affords one of the most valuable confirmations of the new notions of chemistry yet presented to the public; for whilst professing to deny them, he unconsciously and unintentionally adopts their leading principles, and suggests, in his own language, the very notions he intended to disprove. In the following analysis of his paper, we shall have occasion to refer to those peculiarities of chemical language and notation which still constitute an important difference between Dr. Kolbe and ourselves, and which prevent his stating chemical reactions in their simplest and least hypothetical form, or understanding them when so described by others.

The first part of his paper is mainly occupied with a discussion of the theory of etherification, which was suggested some years ago by a series of experiments I performed on the subject. Dr. Kolbe complains of my rejecting too lightly "the old theory" which he considers was one of the main pillars of organic chemistry. Now every chemist knows that at the time my experiments on the subject were published, two different theories of etherification had been proposed by eminent chemists, and each of them was found insufficient for the explanation of the process. I am not aware of having pretended, by my experi-

ments on the subject, to refute either of the old theories of etherification, for they were refuted by facts known to every chemist before ever I worked on the subject. As this is a point of some importance, I must beg leave to be quite explicit, and to explain in a few words what I conceive to have been the position of the question. The two theories of etherification were generally described by their leading principles as the contact-theory and the chemical theory. The latter of these attributed the formation of ether to the action of heat on sulphovinic acid; the former invented the name Contact-force, or Catalysis, and said that the sulphuric acid acted by this force, and not by its usual combining force.

Now, by thus merely inventing a name for the cause of an anomalous decomposition, the contact-theory did not in any degree advance our knowledge of its nature, although some persons have imagined that the difficulty was solved by the invention of this name. The chemical theory was assuredly the first real step towards explaining the process; but it assumed for this purpose facts which were not confirmed by subsequent experiments. In this first reference to the subject, Dr. Kolbe does not inform us which of the two older theories he intends to designate as *the* theory of etherification. If he considers that the formation of ether and water from alcohol is explained by attributing it to a contact-action of sulphuric acid, he must be easily satisfied, for any other conceivable arrangement of the elements would be just as much explained by such a statement. If he considers the chemical theory "a main pillar of organic chemistry," it would be desirable to inform us in what he conceives it to rest, as the supposed fact which constituted its original foundation is known not to exist.

Few experiments are probably so conclusive as to the constitution of bodies, as directly synthetical ones; and Dr. Kolbe justly remarks, that by reasoning consistently on such a basis one would be led to many remarkable conclusions. Thus, when selenious acid is treated with sulphuretted hydrogen, a selenide of sulphur is formed:—

$$Se O_2 + 2 S H = Se S_2 + 2 H O.$$

In like manner (he says) we should be obliged to consider the sulphur precipitated by the action of sulphuretted hydrogen on sulphurous acid, as a compound of sulphur from the two sources:

$$S O_2 + 2 S H = S S_2 + 2 H O;$$

and he very correctly observes, that such conclusions as this would constitute a necessary application of the method of reasoning adopted n my argument on the formation of the compound of oxide of methyl with oxide of ethyl, by the action of iodide of methyl on ethylate of potash. Although it is interesting to find that Dr. Kolbe perceives the necessity of this general use of the method of double decompositions, if it be introduced into our reasonings at all, one is rather surprised to find that he is so little acquainted with the views which he professes to criticise, as to suggest as an idea of his own the very conclusion for which we contend. Thus he goes on to say, that the intermediate ether might reasonably be considered as a compound of oxide of ethyl with oxide of methyl,—a notion to which he conceives I should not be disposed to accede. "I presume, indeed, that Williamson regards the oxides of ethyl and methyl as altogether incapable of uniting into a stable compound, on account of the great similarity of their chemical properties. This prejudice may, however, readily be removed by consideration of analogies from inorganic chemistry. Nobody ever made any difficulty about admitting the existence of chemical compounds of selenium and sulphur, S_2Se, or of chlorine and iodine, ICl_2, ICl_3, which are, however, quite as closely allied to one another as the oxides of ethyl and methyl. Why then should the existence of the compound $C_4H_5O.C_2H_3O$ be less admissible?"

Had Dr. Kolbe taken the trouble of understanding my views before he sat down to write a criticism upon them, he would hardly thus have brought forward, as a new idea suggested by his own reflections, the very conclusion which I had taken much pains in establishing. He alters the atomic weight of oxygen and carbon in my formula, and instead of representing it as containing 3 atoms of carbon of atomic weight 12, he states that it contains twice as many atoms of half the weight:—in like manner, he substitutes 2 atoms of oxygen each weighing 8 for one atom weighing 16. The reasonings by which he tries to convince us that oxide of ethyl *may* combine with oxide of methyl are excellent, but perhaps almost superfluous after I have proved that they *do* combine.

The formation of this compound of the two ethers, I had explained as a process of substitution of methyl for the hydrogen of alcohol through the intermediate action of potassium:—

$$\begin{matrix} C_4H_5O \\ K\ O \end{matrix} + C_2H_3I = \begin{matrix} C_4H_5O \\ C_2H_3O \end{matrix} + KI$$

Now as Dr. Kolbe admits that this compound is formed, and main-

tains that if *analogous* bodies, such as sulphur and selenium combine, the same must be conceived to occur in similar cases between identical bodies like sulphur and sulphur, he cannot without inconsistency deny, that when iodide of ethyl acts on ether-potash, the product is a compound containing both atoms of ethyl, or, in his language, a compound of ether and ether:

$$\begin{matrix} C_4 H_5 O \\ K\ O \end{matrix} + C_4 H_5 I = \begin{matrix} C_4 H_5 O \\ C_4 H_5 O \end{matrix} + K I$$

If an atom of alcohol is represented by the formula $C_4 H_6 O_2$, then an atom of free ether must have the formula $C_8 H_{10} O_2$ containing the elements of two atoms of combined ether; and Dr. Kolbe will find by reference to my papers on the subject, that I distinctly stated from the first, that the relative atomic weights of alcohol and ether may be expressed either by halving the old formula for alcohol ($C_4 H_6 O_2$), or by doubling the old formula for ether ($C_4 H_5 O$).

Vino-methylic ether is a compound of oxide of ethyl and oxide of methyl, just in the same sense as alcohol is a compound of oxide of ethyl and water, and as common ether is a compound of oxide of ethyl and oxide of ethyl. Or take the case of amylic alcohol and the series of ethers obtainable by the replacement of its hydrogen by the radicals methyl, ethyl, propyl, butyl, and finally amyl:

$$\begin{matrix} C_{10} H_{11} \\ H \end{matrix} O_2, \quad \begin{matrix} C_{10} H_{11} \\ C_2 H_3 \end{matrix} O_2, \quad \begin{matrix} C_{10} H_{11} \\ C_4 H_5 \end{matrix} O_2, \quad \begin{matrix} C_{10} H_{11} \\ C_6 H_7 \end{matrix} O_2,$$

$$\begin{matrix} C_{10} H_{11} \\ C_8 H_9 \end{matrix} O_2, \qquad \begin{matrix} C_{10} H_{11} \\ C_{10} H_{11} \end{matrix} O_2.$$

These ethers may all be formed by the action of the iodides of methyl, ethyl, and amyl, on $\begin{matrix} C_{10} H_{11} \\ K \end{matrix} O_2$, the amylate of potash; and Dr. Kolbe's own arguments are quite sufficient to show that the last term of the series must be represented by a formula analogous to those of the previous ones. That analogy is all I contended for. The alcohol itself may be obtained by the action of hydriodic acid on the amylate of potash, just in the same manner as the ethers by their respective iodides; and Dr. Kolbe admits that the alcohol has the above atomic value, corresponding to those of the intermediate ethers. Now let us compare the formulæ of the potash-compounds with water, oxide of methyl, oxide of ethyl, &c., *i.e.* the hydrate, methylate, ethylate,

&c., of that base. Everybody admits empirically that they are represented in their relative atomic weights by the formulæ

$$\begin{matrix}H\\K\end{matrix}O_2,\quad C_2\begin{matrix}H_3\\K\end{matrix}O_2,\quad C_4\begin{matrix}H_5\\K\end{matrix}O_2,\ \ldots\ldots$$

and when they are acted upon by hydriodic acid, everybody admits that in the higher terms of the series, a simple replacement of the potassium by hydrogen takes place, with production of the respective alcohols. But if so, they cannot deny that the process is analogous in the first term of the series; that when hydrate of potash is acted upon by hydriodic acid, the potassium is replaced by hydrogen, as in the other case, with production of the compound $\begin{matrix}H\\H\end{matrix}O_2$:

$$\begin{matrix}H\\K\end{matrix}O_2+HI=\begin{matrix}H\\H\end{matrix}O_2+KI:$$

that is, if they employ the usual formula for alcohol, they must of necessity double that of water, and in like manner those of other simple oxides. In short, it is found that the oxygen in such compounds as hydrate of potash, hydrated oxide of ethyl, &c., is not divisible,—that it is an *atom*; and for that reason, we double the atomic weight of oxygen, in order to avoid formulæ such as the above, which imply that the oxygen consists of two atoms, and we write them,

$$\begin{matrix}H\\H\end{matrix}\text{Θ},\quad \begin{matrix}H\\K\end{matrix}\text{Θ}.*$$

In like manner, the atomic weights of carbon, sulphur, and some other non-metallic elements, are doubled; or the same relation of atomic weights may be attained, as is more usual, by halving the atomic weights of hydrogen and the metals.

It will easily be perceived from these considerations, that the real question at issue between Dr. Kolbe and ourselves has been overlooked by him in the paper I am discussing; for, in accordance with the older habits of reasoning upon chemical reactions, he represents chemical combination as consisting simply in an addition of atoms; and his formulæ for the representation of processes of chemical combination are essentially additive, although numerous reactions in the best-known processes are so clearly proved to consist of double decompositions, that he is obliged to make a partial use of corresponding formulæ; whereas we show that a great number of his supposed pro-

* O = 8, Θ = 16; C = 6, Ⓒ = 12; S = 16, Ⓢ = 32, &c.

cesses of mere combination or mere separation, really consist of double decompositions, and believe that all processes of chemical action will similarly be reducible to that method when the steps of which they consist are accurately known. Laurent showed some years ago,* that so-called free chlorine ought to be considered as a compound of two elementary atoms of that element, and the same of hydrogen; so that when 2 vols. chlorine combine with 2 vols. hydrogen, the 4 vols. of hydrochloric acid are to be considered as 2 atoms of that compound, formed by double decomposition between the elementary gases. I would particularly recommend the papers of that eminent chemist to Dr. Kolbe's perusal, as they would probably save him many surprises to which he would otherwise be exposed. The same applies to M. Gerhardt's theoretical papers, and to some papers by Mr. Brodie on the same subject, with which Dr. Kolbe can hardly be acquainted.

Dr. Kolbe disclaims any intention of refuting my results on the constitution of alcohol and ether, although he does not consider them proved. The formation of amylovinic ether by the action of sulphuric acid on a mixture of amylic and vinic alcohols, may, he says, be as well explained by the old theory. It is a pity the author did not attempt to show how this might be done, as he would probably thus have been led to suggest, as an original idea, the explanation I have given of the process; for he goes on to show how my equation for the formation of vinic ether by the action of sulphovinic acid on alcohol may be rendered by the old theory. He thus translates my equation:

$$C_4H_5O\,.\,SO_3 + HO\,.\,SO_3 + C_4H_5O\,.\,HO = 2(C_4H_5O) + 2(HO\,.\,SO_3).$$

Now the equation thus written is incorrect according to any theory whatever. No theory ever justified the use of the sign of addition in two perfectly different senses in one equation; and when this fault is corrected, the equation does not belong to any theory which existed previous to my experiments; for it attributes the reaction to a change of place between ethyl in sulphovinic acid and hydrogen in alcohol, —the very point which I proved in contradiction to the previous views. But in his next sentence Dr. Kolbe unfortunately gives proof of not understanding the meaning of the equation, for he says: "Whatever hypothesis we adopt respecting the formation of ether by sulphuric acid—unless we regard contact-action as the cause—it will always remain inexplicable how sulphovinic acid can be reproduced at the same

* Ann. Ch. Phys. [3] xviii. 295.

temperature at which this same sulphovinic acid resolves itsel (zersetzt sich) into ether and sulphuric acid." In one sentence, the author asserts that the formation of ether by double decomposition between sulphovinic acid and alcohol is consistent with the old theory; in the next, he refers to the formation of ether by the action of heat on sulphovinic acid, as a *fact* to be explained by contact-force.

The author then enters on the consideration of the theory of atomic motion, as illustrated by the spontaneous interchanges of hydrogen and ethyl, first in one direction, then in the other. It is not to be expected that Dr. Kolbe would admit this generalisation, since he does not admit the fact of etherification, of which it is a general expression; I must, therefore, beg to be excused from entering into any explanation of my views on the subject. Dr. Kolbe endeavours to apply and illustrate the principle of atomic interchanges, which he seems to conceive must take place much more easily between particles which are far apart, as in a gas, than between those which are comparatively near together, as in a liquid. And again he asks: What can be the difference between a mixture of chlorine and hydrogen, and the compound of those elements, if in the compound the atoms of hydrogen are constantly exchanging their combined atoms of chlorine? The answer is simply, that in the *mixture* of the two gases the atoms of hydrogen are *not* combined with chlorine-atoms, and cannot therefore exchange them. Again, he inquires how it is that a mixture of sulphovinic acid and alcohol does *not* contain sulphuric acid, which it ought to do if ethyl and hydrogen were changing places. Anybody could inform him that the fact he states is incorrect, for the mixture of sulphovinic acid and alcohol *does* contain some sulphuric acid and ether; and we are the more surprised at Dr. Kolbe's forgetting this circumstance, from his having affirmed, at an earlier part of his paper, that the reproduction of sulphuric acid from sulphovinic acid is a part of the (contact-) theory of the process of etherification. He says that chloride of ethyl ought, according to our theory, to precipitate alcoholic nitrate of silver, and would probably find the reaction occur, though slowly, for it is well known to take place with the iodide of ethyl.

In pursuing our analysis of his paper, we must now return with Dr. Kolbe to the subject of etherification. In illustration of the facility with which the principle of double decomposition explains the formation of ether, I described, in a German translation of one of my papers on the subject, the reaction of chloride of zinc upon alcohol,

showing that its action might be explained by a series of double decompositions, perfectly analogous to those I had proved to occur in other instances.

The author says that the former ether-theory gives as simple an interpretation of the reaction, and, in evidence of this, proceeds to write under my equations others which agree with them in attributing the result to the formation of chloride of ethyl and zinc-alcohol, and to a double decomposition between these compounds, but differ from them by the introduction of certain inconsistencies which cannot be seriously maintained, even by Dr. Kolbe. The first equation is a literal transcript of mine, halving the atomic weights which I had employed for carbon and oxygen, and accordingly taking twice as many atoms of these elements. It states that when chloride of zinc reacts on alcohol, an exchange of hydrogen and zinc may occur, forming hydrochloric acid and one atom of zinc-alcohol (a compound of ether with oxide of zinc). The second equation shows that by the action of hydrochloric acid on alcohol, an exchange of hydrogen and ethyl takes place, forming chloride of ethyl and *two* atoms of water. In these reactions, zinc, hydrogen, and ethyl are admitted to be analogous bodies, to the extent of being able to replace one another. The first equation acknowledges the replacement of one of the three in alcohol by another, without disturbing the arrangement of the other elements of the alcohol. The second equation asserts, that when one of the three is replaced by another, the remaining elements of the alcohol *divide*. Both are perfectly analogous cases of interchange of basic constituents between alcohol and a chloride; yet in the second our author imagines a splitting up of the atom of oxide produced into two atoms, whereas in the first he acknowledges that they remain combined. The third equation contains an error similar to that of the second; for he there misstates the atomic weight of ether, just as in the second that of water was stated incorrectly. In fact, the equations are an erroneous version of my own theory, and have no connection (unless in Dr. Kolbe's imagination) with any other.

After disposing of the theory of etherification, on which his remarks seem prefatory to the main subject of his paper, Dr. Kolbe at length introduces the question of the constitution of acetic acid and its homologues.

His first argument against the othyl-theory consists in showing that a consequence which he deduces from it is disproved by experiment. Condensed into a few words, the reasoning runs thus:—Acetic acid is

said to be water in which half the hydrogen is replaced by othyl. If this is true, othyl ought to go to the same pole as hydrogen when the compound is broken up by electrolysis. But experiment proves the contrary. Now in attributing such a function to the radical othyl, the author misrepresents the theory he professes to test. He ought to have known that I never attributed to that radical the same functions as those which belong to hydrogen; but that the opposition of functions which the two bodies are known to possess is attributed to their difference of properties rather than to any difference of position. Dr. Kolbe can hardly have imagined that I considered the properties and functions of acetic acid the same as those of water, or the same as those of hydrate of potash, which belong to the general type. However, in case he may have formed so peculiar an opinion, it may be as well to inform him, that when a chlorous radical replaces hydrogen in water, it is not converted into hydrogen, and does not assume its functions, but gives rise to a compound of more acid properties; when a basylous radical replaces hydrogen in water, the compound formed is no longer water, but a stronger base; and that when half the hydrogen in water is replaced by a chlorous radical, the other half by a basylous one, the compound is a salt, which, on decomposition by the current, really sends its chlorous constituent in an opposite direction from its basylous component, though both were contained in the place of hydrogen.

Dr. Kolbe says that the argument just analysed is sufficient to disprove my acid-theory; and in the belief of having succeeded in that much-desired object, he proceeds to explain his own previously published experiments and views on the subject. He appears to be rather hurt at the comparatively small amount of notice those views have obtained of late years, and charges me with having specially ignored them. It is perfectly true that in publishing my views on the constitution of the organic acids, I made no mention of Dr. Kolbe's theories on the subject; and I must confess it is with regret that I now find myself compelled by his challenge to abandon that reserve. For I hoped that he would spontaneously abandon formulæ which, both as regards substance and form, are perfectly inadmissible, and which greatly perplex a subject by no means intricate or difficult in itself. The chief peculiarity of Dr. Kolbe's method of representing chemical compounds, consists in the very frequent use he makes of undefined symbols; indeed, there is hardly any other chemist who does this in the same degree as himself. Take, for instance, his formula for acetic acid—

$$(C_2 H_3)\hat{}C_2, O_3 . HO.$$

The elements $(C_2 H_3)$ are supposed to be combined in the form of methyl, and are accordingly shut off by a parenthesis from the remaining elements of the compound; C_2 are united with them by a symbol which Dr. Kolbe has invented for the purpose, and which M. Gerhardt calls a buckle; O_3 are supposed to be united with the methyl and carbon in some manner different from either of the preceding, and a new sign (comma) is accordingly used; H and O are united together in a manner different from either of the above-mentioned, and simple juxtaposition is the sign for this fourth mode of combination; lastly, the water (ready formed) is joined on to the elements of the anhydrous acetic acid by the fifth sign (full stop). Now if these or any other differences of combination were really known to exist among the elements of acetic acid, it might be a question whether it would not be more useful to describe them in words of known meaning, rather than to invent arbitrary and undefined signs for them. But not one of them can be shown to have any existence, so that the formula of one of the simplest of organic bodies is confused by the introduction of unexplained symbols for imaginary differences in the mode of combination of its elements.

My objections to Dr. Kolbe's formulæ may be described under the following heads:—1. They give a wrong atomic weight for the acetic acid series and other monobasic acids; for, water being represented by the formula HO, acetic acid contains empirically $C_2 H_2 O_2$, and not double that number of elements, as Kolbe's formula states. 2. Any formula or other description of an organic body is of course only applicable to it under those conditions in which it retains its peculiar form and properties. Thus, a formula for acetic acid cannot apply to it beyond that temperature at which the compound undergoes decomposition; for beyond this limit, the elements are no longer arranged in the form or with the properties of acetic acid. Now Dr. Kolbe's theory does exactly the reverse of this; for it assumes in acetic acid an arrangement of elements which is never known to occur until an acetate is subjected to destructive influences. His definition of acetic acid is only true of the elements of that body when they depart from the arrangement which constitutes acetic acid.—3. This theory of acetic acid fails, or rather omits entirely, accounting for the formation of chloride of othyl and anhydrous acetic acid.—4. It shows no connexion between acetic acid and alcohol, from which it is formed by the substitution of oxygen for hydrogen:

$$\overline{C}_2\,H_6\,\overline{O}+\overline{O}_2=\overline{C}_2\,H_4\,\overline{O}_2+H_2\overline{O}$$

In fact, it accounts for none of the transformations within the type of the acetates, and begins exactly where a correct theory would end.

I regret that my strictures cannot in justice stop at these negative charges, which merely show that Dr. Kolbe has failed in establishing an admissible theory of the constitution of acetic acid. For he has greatly contributed to the development of what must be acknowledged to be the chief defect of our present system of chemistry. Whilst others were striving to simplify the method of explaining chemical changes, by analysing or eliminating those vague and ill-defined terms which necessarily arise in the infancy of a science, Dr. Kolbe has been moving in the opposite direction, and has been confusing his own ideas and those of his countrymen, by the introduction of perfectly unmeaning signs for the representation of imaginary facts and equally unreal distinctions. For instance, his formula for acetic acid says that half its carbon is combined with part of its hydrogen, as methyl, and that the other half is joined on to this methyl in some mysterious way (illustrated by a buckle); that three atoms of oxygen are joined in some different manner to the carburet of methyl, and that water (ready formed) is united to this oxycarburet. Now if this method of giving arbitrary signs to the combining forces of imaginary constituents were to supersede a description of the leading properties of compounds, and a comparison of them with those of other compounds according to their classification, chemistry would soon cease to be a science. It would be just as reasonable to describe an oak-tree as composed of the blocks and chips and shavings to which it may be reduced by the hatchet, as by Dr. Kolbe's formula to describe acetic acid as containing the products which may be obtained from it by destructive influences. A Kolbe botanist would say that half the chips are united with some of the blocks by the force *parenthesis*; the other half joined to this group in a different way, described by a *buckle*; shavings stuck on to these in a third manner, *comma*; and finally, a compound of shavings and blocks united together by a fourth force, *juxtaposition*, is joined on to the main body by a fifth force, *full stop*. The general use of unmeaning signs has become so habitual to Dr. Kolbe, that whenever anything has to be explained, he performs the task to his own satisfaction by inventing a sign for its unknown cause. He fancies that equations explaining a result by a given series of decompositions belong to a different theory when their unit is altered and their form changed, so as to admit of the same

sign being used in different senses. He thinks that the word "contact-force" gives a better explanation of the process of etherification than a description of the successive steps of which the process has been proved to consist. Signs and words are doubtless indispensable means for the expression of facts or thoughts; but Dr. Kolbe uses them instead of facts, and as a substitute for ideas.

Dr. Kolbe proceeds to argue in favour of his idea of acetic acid containing methyl and carbon as a compound radical, $(C_2 H_3)^{\frown}C_2$, and informs us that he sees in the valuable additions which our knowledge of acetic acid has received since this view was brought forward, nothing but further evidence of its truth. He does not, however, explain in what manner the formation of chloride of othyl and of anhydrous acetic acid, and of their various reactions producing numerous bodies containing the radical othyl (all discovered since his theory was promulgated), can be considered as confirmations of the notion of his carburet of methyl. He says that carbon may very well be conceived to form a compound radical with methyl, since selenium, tellurium, and arsenic are known to do so. Carbon, however, possesses no such analogy with those elements that it must be supposed to combine in the same way as they do; but on the contrary, behaves so differently from them in most cases, that it may be concluded it would do so in this instance also. If part of the carbon in acetic acid were replaced by another element, that fact would be no proof that the carbon had been contained in two different forms in the original acid, any more than the replacement of part of the hydrogen in ethyl by chlorine would be any proof that there were two sorts of hydrogen in the ethyl before that substitution.

Dr. Kolbe says: "Since Gerhardt and Chiozza's recent and very important researches have proved the correctness of Liebig's and Wöhler's original benzoyl-theory, and it can therefore scarcely be doubted that an oxygenised radical occurs in acetic acid and other acetyl-compounds, the old acetyl $(C_2 H_3)^{\frown}C_2$ naturally presents itself as the ultimate radical, and the group $(C_2H_3)^{\frown}C_2O_3$ as the proximate radical of these compounds; the latter might be called *acetoxyl*." Now Dr. Kolbe cannot fail to recollect that Gerhardt and Chiozza prepared compounds containing othyl exactly in the same manner as they prepared others containing benzoyl, and their researches prove the correctness of the othyl-theory by the same reactions which are admitted to prove the correctness of the benzoyl theory. But they even did more in proof of the othyl-theory than what Dr. Kolbe admits to be proof of the benzoyl-theory, for Gerhardt prepared the chloride of othyl from an acetate by

the pentachloride of phosphorus,—a reaction which had been discovered previously in the case of benzoyl by Cahours, and which is the same as that by which the chlorides of the best-known radicals, such as methyl, ethyl, amyl, &c., are prepared. Our author thus acknowledges the decisive character of evidence which, applied to the question at issue (acknowledged analogous), proves the very fact which he intended upsetting.*

The author alludes to Gerhardt's discovery of monobasic anhydrous acids, and seems disposed to deny the conclusions which have been drawn regarding their constitution from observations of boiling points, densities of vapours, &c. He then proceeds to suggest experiments which in his opinion would be of great interest, especially the preparation of anhydrous acetic acids in which uneven numbers of atoms of hydrogen in the group $\begin{matrix}\mathrm{C_2H_3O}\\ \mathrm{C_2H_3O}\end{matrix}\mathrm{O}$ are replaced by chlorine. The existence of a body such as one of these, would, he admits, be inconsistent with his formula for acetic acid, which admits only three atoms of hydrogen. It is singular Dr. Kolbe should not have perceived that the action of chloride of othyl on chloro-acetate of potash will give rise to an anhydrous acetic acid in which three out of the six atoms of hydrogen will be replaced by chlorine—

$$\mathrm{C_2H_3O.Cl} + \begin{matrix}\mathrm{C_2Cl_3O}\\ \mathrm{K}\end{matrix}\mathrm{O} = \begin{matrix}\mathrm{C_2Cl_3O}\\ \mathrm{C_2H_3O}\end{matrix}\mathrm{O} + \mathrm{ClK}$$

exactly in the same way as the chloride of othyl produces in its action on benzoate of potash, the benzoate of othyl; nor is it very clear in what respect the existence of the former intermediate acid would be more satisfactory in disproof of his formula than the latter one, and the others of analogous constitution discovered by Gerhardt. His remarks on the subject of the possible decomposition of ethylate of potash by the electric current are precisely the equivalent of those on the corresponding decomposition of the acetate; and I am not aware that in describing ethyl in that compound as acting the part of a chlorous radical, I have given any reason to conclude that it should act in electrolysis like a base.

One important subject on which the ideas of some chemists at the present time are particularly confused, is the doctrine of chemical

* Since writing the above, I perceive that in the version of Dr. Kolbe's paper published in Liebig's Annalen, xc. 56, the formula of othyl with altered atomic weights $[(C_2H_3)^{\frown}C_2O_2]$ is here given instead of that of anhydrous acetic acid. [A. W. W.]

equivalents; and this confusion arises in great measure from a careless use of the same word in different meanings. Dr. Kolbe in the course of his paper touches on this point, and brings forward in connection with it what he considers a contradiction to my theory. Before considering his remarks on this subject, I must beg leave to remind the Society of the atomic explanation which I suggested for polybasic acids. When in two atoms of water half the hydrogen of each is replaced by a chlorous radical, the acid produced is monobasic or bibasic, according to the *atomic* weight of the radical. For example, take *equivalent* quantities of peroxide of nitrogen N_2O_4 and sulphurous acid SO_2; that is, quantities susceptible of replacing equal amounts of hydrogen; and let the peroxide of nitrogen replace two atoms of hydrogen in two of water $\begin{matrix} H \\ H \end{matrix}O\ \begin{matrix} H \\ H \end{matrix}O$; let the sulphurous acid also replace two atoms of hydrogen in two of water, forming respectively nitric acid $N_2O_4\begin{matrix} H \\ H \end{matrix}O_2$ and sulphuric acid $SO_2\begin{matrix} H \\ H \end{matrix}O_2$. The first product will consist of two atoms of the composition $N\begin{matrix} H \\ O_2 \end{matrix}O$, the second of one atom only, because N_2O_4 is divisible into two atoms NO_2, whereas SO_2 is indivisible, two atoms of the former being equivalent to one atom of the latter radical. An atom of the bibasic radical, on replacing two atoms of hydrogen, holds together the elements with which the hydrogen had been combined; but when the same amount of hydrogen is replaced by a monobasic radical, such as peroxide of nitrogen, each of the two atoms acts by itself, replacing one of hydrogen. Basylous radicals act in a perfectly similar manner. The atoms of some of them can replace more hydrogen than those of others, *i. e.* have a different equivalent value from them; and there are some metals susceptible of replacing hydrogen in two or more definite proportions,—that is, of altering their equivalent. Thus, tin in the protochloride may be considered as replacing one atom of the hydrogen of hydrochloric acid; in the bichloride, where the same weight of metal is combined with twice as much chlorine, it replaces twice as much hydrogen. But although the equivalent or substitution-value of the metal is different in these two compounds, its atomic weight is the same. Again, iron, in its protoxide, has an equivalent or substitution-value

of 28; for one part of hydrogen is replaced by that weight of the metal, and in an atom of water one or both atoms of hydrogen may be thus replaced. But in the sesquioxide of iron, only two-thirds as much of the metal are found in combination with a like amount of oxygen; for two atoms of iron replace and are equivalent to three of hydrogen.*

Now Dr. Kolbe objects to M. Gerhardt's using a symbol to express this well-known difference in the combining proportions of iron in its two oxides and their respective salts. He attributes to Gerhardt formulæ for the neutral benzoates of the two oxides of iron, in which the basic hydrogen in benzoic acid is replaced, first by iron with its greatest combining proportion, and then by two-thirds that quantity of the metal,—formulæ which represent strictly the combining proportions of the elements in those two salts. Now I must confess that while fully appreciating the logical importance of being able by such formulæ to represent the composition of salts without resorting to any hypothetical notion, and from the sole point of view of equivalence or replacing power, I am disposed to prefer, for most purposes, an atomic representation of their constitution, as the molecular weights of the salts, or, I may say, their atomic weights, are thus represented, and their polybasic or polyacid character described. Instead of using the symbol of iron as representing merely its equivalent or substitution-value, and accordingly indicating the variation of that substitution-value by a change of symbol, I prefer the uniform adoption of the *atomic* weight in the several classes of salts.

Thus, if $Bz = \overline{C}_7 H_5 \overline{O}$, we shall have $\overset{Bz}{fe}\,\overline{O}$ and $\overset{Bz_3}{fe_2}\,\overline{O}_5$ as the formulæ of the proto- and sesqui-benzoate of iron. If these formulæ do not agree with Dr. Kolbe's ideas on the subject, he must at least acknowledge that they are perfectly consistent with my method of representing other products of substitution of water; and that the fact of the atomic weight of iron being unchangeable, whilst its equivalent value alters, or, in other words, the fact of an atom of iron sometimes replacing one of hydrogen, sometimes two of iron replacing three of hydrogen, is *the only* explanation of the union of three atoms of benzoic acid by the sesquioxide into what we may call a triacid salt. The author will no doubt see by them why the com-

* In connection with this subject, see Dr. Odling's important paper "On the Constitution of Acids and Salts," page 1 of this volume.

pounds are not possible which he correctly suggests might occur if Gerhardt's formulæ of the benzoates were correct; for, as the equivalent value of potassium is not known to vary in any of its salts, it could not be expected to pass over into the type of sesquioxides, and in precipitating iron-alum must necessarily throw down the whole of each atom of sesquioxide, reproducing a common protosulphate.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

ANNIVERSARY MEETING, March 30, 1854.

COLONEL PHILIP YORKE, President, in the Chair.

The Report of the Council and the Audited Account of the Treasurer were read (*vide* pp. 144 and 159).

The Meeting then proceeded to the election of Council and Officers for the ensuing year, and the following gentlemen were declared to have been duly elected :—

PRESIDENT.

Colonel Philip Yorke, F.R.S.

VICE-PRESIDENTS,
(WHO HAVE FILLED THE OFFICE OF PRESIDENT).

W. T. Brande, F.R.S. C. G. B. Daubeny, M.D., F.R.S.
Thomas Graham, F.R.S.

VICE-PRESIDENTS.

H. Bence Jones, M.D., F.R.S. Robert Warington, Esq.
G. D. Longstaff, M.D. A. W. Williamson, Ph.D.

SECRETARIES.

B. C. Brodie, F.R.S. Theophilus Redwood, Ph.D.

FOREIGN SECRETARY.

A. W. Hofmann, Ph.D., F.R.S.

TREASURER.

Robert Porrett, F.R.S.

OTHER MEMBERS OF THE COUNCIL.

Thomas Anderson, M.D.	W. A. Miller, M.D., F.R.S.
Dugald Campbell, Esq.	Hugh Lee Pattinson, F.G.S.
Warren De la Rue, Ph.D., F.R.S.	John Stenhouse, LL.D., F.R.S.
J. H. Gladstone, Ph.D., F.R.S.	Thomas Taylor, Esq.
William Herapath, Esq.	John Thomas Way, Esq.
Charles Heisch, Esq.	George Wilson, M.D., F.R.S.E.

The thanks of the Society were voted to the President, Officers, and Council, for their services during the past year.

April 3, 1854.

Colonel Philip Yorke, President, in the Chair.

August Kekulé, Ph.D., and Reinhold Hoffmann, Esq., were elected Associates of the Society.

Mr. J. T. Way communicated to the Society the results of his investigations "On the influence of certain parts of the soil in separating saline and other matters from their solution in water, and in absorbing and fixing the valuable constituents of manure, so as to present them in an available form to the roots of plants."

April 17, 1854.

A paper was read "On the Composition of a specimen of Atacamite from the province of Copiapo, Chili," by Frederick Field.

May 1, 1854.

COLONEL PHILIP YORKE, President, in the Chair.

Robert Railton, Esq., of University College, and Patrick Duffy, Esq., of Belfast, were duly elected Fellows of the Society.

Dr. H. Bence Jones delivered a discourse "On the Quantitative Examination of Solutions of different varieties of Sugar by Soleil's Saccharometer."

May 15, 1854.

PROFESSOR GRAHAM, Vice-President, in the Chair.

The following donations were announced:—

"Literary Gazette:" four numbers, from the Publishers.

"Journal of the Society of Arts:" four numbers, from the Society.

"Journal of the Photographic Society:" four numbers, from the Society.

"Bulletin de la Société Vaudoise des Sciences Naturelles:" four numbers.

"Proceedings of the Royal Society:" from the Society.

"Journal of the Franklin Institute:" from the Institute.

"Pharmaceutical Journal for May:" from the Editor.

H. W. Müller, Ph.D., 110, Bunhill Row, and Charles Greville Williams, 3, Oxford Court, Cannon Street, were duly elected Associates of the Society.

The following papers were read:—

"On the occurrence of Ozone and Peroxide of Hydrogen in the Electrolysis of Sulphuric Acid:" by Heinrich Meidinger.

"On the Corrosive Action of Sugar on Iron and other Metals:" by Dr. J. H. Gladstone.

June 5, 1854.

COLONEL PHILIP YORKE, President, in the Chair.

The following donations were announced:—

"The Journal of the Society of Arts:" two numbers, from the Society.

"The Journal of the Photographic Society:" two numbers, from the Society.

"The Pharmaceutical Journal for June:" from the Editor.

"The Quarterly Journal of the Geological Society:" from the Society.

"The Literary Gazette:" two numbers, from the Publishers.

"On the Homœomorphism of Mineral Species of the Trimetric System; and an Appendix to ditto:" by James D. Dana.

"Contributions to Chemical Mineralogy:" by James D. Dana.

Dr. E. Frankland delivered a discourse "On the Technological History of Wood as a Raw Material."

June 19, 1854.

Colonel Philip Yorke, President, in the Chair.

The following papers were read:—

"Preliminary Notice on the Action of Ammonia on the Oils and Fats:" by Thomas H. Rowney, Ph.D.

"On the Action of Iodine on Calomel:" by Dr. R. M. Glover.

"On an unexpected source of Nitrobenzoyl:" by Arthur H. Church.

"On the Substitution-Compounds obtained by the Action of Nitric Acid on Cotton:" by Edward Ash Hadow.

ANNIVERSARY MEETING,

MARCH 30, 1854,

COLONEL PHILIP YORKE, F.R.S., PRESIDENT,

IN THE CHAIR.

THE following Annual Report of the Council was read by the President:—

The Council are happy to be able to announce on this occasion, which is our fourteenth Anniversary, that the Society is in a prosperous condition. The number of Fellows at the last Anniversary were:—

Resident and Non-resident	241
Deduct Deaths, Withdrawals, and Removed being in arrear	7
	234
Add elected since	13
	247

From our Foreign list the Society has lost two by death during the past year, both of them men eminently distinguished in advancing the science which is the object of this Society, and claiming a notice in this Report.

Leopold Gmelin belonged to a family which for four generations had been actively engaged in the pursuit of Chemistry. Johann Georg Gmelin, apothecary at Tübingen, who was born in 1674 and died in 1728, had three sons, all of whom devoted themselves to Chemistry and the allied sciences. Johann Conrad Gmelin (born 1707) was a physician and apothecary at Tübingen; his grandson, Christian Gottlob Gmelin (born 1792), is now Professor of Chemistry at the same place. Johann Georg Gmelin the younger (born 1709) practised as a physician at St. Petersburgh, where he was made Professor of Chemistry and Natural History, but is chiefly

known by his travels in Siberia (1738 to 1745); he afterwards returned to Tübingen, where he was appointed Professor of Chemistry and Botany, and died in 1755. The third son, Philip Friedrich Gmelin (born 1722), succeeded the last-mentioned in his Professorship, and died at Tübingen in 1768; he was the father of Johann Friedrich Gmelin (born 1748), Professor of Natural History and Botany at Tübingen, and afterwards of Chemistry at Göttingen, and the grandfather of the distinguished man who forms the subject of this notice.

Leopold Gmelin was born at Göttingen on the 2nd of August, 1788. From 1799 to 1804 he attended the Lyceum at Göttingen, and in the summer of 1804, his father's lectures on Mineralogy. In the autumn of the same year, he went to Tübingen, where he practised chemical manipulation in the pharmaceutical laboratory of his near relation, Dr. Christian Gmelin (the son of Johann Conrad Gmelin, and father of Christian Gottlob Gmelin), and attended Killmeyer's lectures on Chemistry.

In the autumn of 1805 he returned to Göttingen, where he devoted himself with zeal to all branches of medical science, but especially to Chemistry, for which he attended Stromeyer's lectures: he also studied mathematics. After passing a distinguished examination, he went, in the summer of 1809, to Würtemburg, and thence to Switzerland, which he traversed in all directions, hammer in hand. From the autumn of 1809 to Easter 1811 he remained in Tübingen, and then went to Vienna, where he visited the hospitals, and carried out, in Jacquin's laboratory, the greater part of the experiments which form the basis of his Doctor-dissertation "On the Black Pigment of the Eye." He left Vienna in the spring of 1812, and went to Italy, where he remained till the spring of 1813,—chiefly at Naples, but for some time also at Rome. The observations and collections made in these journeys supplied the chief material of the chemico-mineralogical investigations which formed the subject of his "Habilitation-schrift" at Heidelberg.

On his way back to Göttingen, he staid some time at Heidelberg, where the Professor of Chemistry, George Succow, being then recently dead, Gmelin was encouraged to give lectures on Chemistry. Availing himself of the opportunity thus presented, he obtained the *venia docendi* in Heidelberg, spent the remainder of the summer at Göttingen, making the necessary preparations for his new duties, and in the autumn of the same year began his career as an academic teacher in Heidelberg, which he afterwards pursued with zeal and success for nearly forty years. Twelve months afterwards he was appointed

Extraordinary Professor of Chemistry. His celebrated "Handbook of Chemistry" was then already begun. In the autumn of 1814, he went to Paris, and occupied himself chiefly with practical researches in Vauquelin's laboratory. Two years afterwards he won the heart and hand of Luise Maurer, the daughter of a clergyman in the neighbourhood of Heidelberg, and thereby laid the foundation of a domestic happiness which continued without interruption to the end of his days. By this marriage, which was blest with three daughters and a son, Gmelin became completely domesticated in Heidelberg; and for the sake of his wife, who was unwilling to quit the beautiful scenes of her home, he even declined the honourable and lucrative appointment of Professor of Chemistry at Berlin, whither he was invited in 1817, to succeed Klaproth, who died in that year. He was soon afterwards made ordinary Professor of Medicine and Chemistry at Heidelberg. Some years afterwards, in 1835, he declined, for similar reasons, an equally honourable and advantageous summons to fill the Chair of Chemistry at Göttingen, preferring to remain in his adopted home, although his emoluments there were much less than they would have been either at Göttingen or at Berlin.

In 1841 he made an excursion to Oldenburg, where his eldest daughter had been some months married, and there, on the 1st of October, he celebrated his "silberne Hochzeit," the twenty-fifth anniversary of his marriage. His hair had then become grey, but his frame still retained all the vigour of youth.

But he rarely indulged himself with recreations like this journey; indeed, in the latter portion of his life he was so completely engrossed with the gigantic labour of preparing the fourth edition of his "Handbook," that he became quite neglectful of his health. Often, after many weeks' untiring exertion in the lecture-room, in the laboratory, and, most of all, at the writing-desk, he would barely allow himself an hour's recreation in the twilight for a walk over the neighbouring hills.

In 1848, he had an attack of paralysis, which though it only deprived him for a while of his power of action, nevertheless destroyed the freshness and vigour of his manner. From that time a dark cloud seemed to overshadow him, ready at any moment to discharge the storm. But he still worked at his "Handbook" with untiring assiduity, as shown by the volumes which have since appeared. In 1850 he was again attacked by paralysis, which obliged him to resign his professorial functions. He still, however, remained active in the cause of science, and laboured earnestly at the second volume of the

"Organic Chemistry," which he completed in May 1852. But from that time his powers, both mental and bodily, rapidly declined; an insidious disease of the brain was steadily gaining ground; and soon there was nothing left of Leopold Gmelin but the shadow. Even in this state he exhibited the greatest anxiety about the appointment of a worthy successor to his Professorship; and when he heard that Bunsen was to succeed him, his suffering countenance was lighted up with joy, as if he had received a positive assurance of his own recovery. In the spring of 1853 it became evident that his end was approaching, and he died on the 13th of April, in the 65th year of his age.

The most striking feature of Gmelin's character was his thorough conscientiousness, and the purity and truthfulness of mind thence arising. He was, in the fullest sense of the word, an *anima candida*, —a man never satisfied with anything that may just pass for truth, but striving earnestly after that which is really true. This principle regulated his scientific inquiries, his conduct as a teacher, and, most of all, his moral and social character. In his scientific researches, he thought only of science,—not of anything external to it. Free from ostentation, and rather keeping in the background than putting himself forward, he never sought for effect or transient display, but only for solid facts and the real progress of knowledge. As a teacher, he exhibited the same absence of display and pretension, and, though not particularly eloquent, he won the confidence of his pupils by the depth and conscientiousness of his teaching, and the paternal solicitude with which he watched their progress.

But it was in his family circle—in the midst of his children and grandchildren—that his character shone forth in all its beauty. His fresh, harmonious, unsophisticated nature, enabled him at once to win the hearts of children; he played with them like one of themselves, was never tired of giving advice and instruction, and showed the greatest delight at any remark or question which exhibited intelligence or desire of knowledge. He felt deeply all the joys and griefs of those who were dear to him; no sacrifice for their sakes was too great; and, while he gave them everything, he exacted nothing for himself. The same kind, truthful spirit and generous sympathy he likewise extended to his friends, among whom were a great number of excellent and distinguished men from all circles of life. Such a man was sure to gain the ready confidence of all who approached him. There was no artificial or assumed manner to separate from that which was real and permanent in him,—no conventional medium to be looked through in order to arrive at his real nature. His polite-

ness, which he never laid aside even in the most familiar household intercourse, was the outpouring of a friendly and benevolent spirit, and required no peculiarity of manner to recommend it; it went hand in hand with the almost excessive modesty which was one of the greatest ornaments of his character.

To the world at large, however, Gmelin is known only by his scientific discoveries and writings. His original researches in Chemistry are numerous; they are all of high character, and as complete as the means of investigation existing at the time of their publication would admit. His Doctor-dissertation, "On the Black Pigment of the Eye," was published in 1812; his Habillitation-schrift, "On Hauyne and minerals related to it, together with geognostic observations on the mountains of ancient Latium," in 1814. In 1820, he undertook, in conjunction with Tiedemann, a series of experiments on Digestion; and in 1826 and 1827, these two philosophers published their celebrated research, entitled "Die Verdauung nach Versuchen."

But the greatest service which Gmelin rendered to science,—a service in which he surpassed all his predecessors and all his contemporaries,—consists in this:—That he collected and arranged in order all the facts that have been discovered in connection with Chemistry. His "Handbuch der Chemie" stands alone. Other writers on Chemistry have indeed arranged large quantities of material in systematic order; but for completeness and fidelity of collation, and consecutiveness of arrangement, Gmelin's "Handbook" is unrivalled. It is quite in accordance with the extraordinary simplicity and truthfulness of his nature, that in this work, as in his other writings, he disdains all ornament of style, and aims at truth alone, which everywhere gushes out towards the reader like water from a rock. In the endeavour to depict with accuracy the almost boundless field of chemical science, he condenses all the known facts in the smallest possible space, but nevertheless contrives to present a complete picture of them. His accurate acquaintance with chemical science in all its breadth and depth, his comprehensive knowledge of languages, his untiring industry, and a tenacity in carrying out a plan once adopted, which shrank from no difficulties, fitted him above all others for carrying out such an undertaking. The wonderful strength of his memory, and a rare power of comprehension and description, enabled him to review in thought a large quantity of material, and mark out its principal divisions, after which he carefully distributed the several fragments of matter in their proper places. Detached and

long-forgotten observations of other chemists were often indebted to Gmelin for first giving them their true value, inasmuch as he put them in their proper places, and showed their connection with other observations. While other large Manuals of Chemistry,—that of Berzelius for example,—give merely the subjective view which the author takes of the science, stating of the observations of other chemists only so much as he may consider true and valuable, and the consequences which he may be inclined to deduce from them, often in opposition to the opinions of the authors themselves,—Gmelin sets the example of putting together, in a purely objective view, and on the authority of the several investigators, all that has been observed within the domain of Chemistry,—not, indeed, withholding his own opinions, but placing them side by side with those of others, and never suppressing the latter. Other chemical manuals may, indeed, be compared to sketches made by hand, in which the fidelity of representation depends altogether upon the idiosyncrasy of the delineator; but Gmelin's "Handbook," in each of its editions, is a Daguerreotype of the science at the time of its appearance, and gives the pith of individual chemical investigations with such fidelity and completeness, as in many cases to enable chemists to dispense with reference to the original memoirs. Moreover, it has often directed attention to deficiencies and contradictions, and thus given rise to new investigations. It has been widely influential in extending an accurate knowledge of Chemistry, not only in Germany, but wherever the science is cultivated. The first edition of this great work, which appeared in 1817–1819, included in a comparatively small space the whole extent of chemical science as then known; the fourth, which was the last prepared by Gmelin himself, was published from 1843 to 1852, and comprehends, in five well-filled volumes, the whole of Inorganic Chemistry, but, unfortunately, only a small part of Organic Chemistry. It is from this edition that the English translation, now in course of publication under the auspices of the Cavendish Society, is made. The additions made by the translator bring the work down to the existing state of chemical science at the time of publication of each volume.

Auguste Laurent was born on the 14th of November, 1807, at La Folie, near Langres (Haute Marne). He was the second of four sons. His father, who was a wine-merchant, intended him to succeed to the business, and required of him to learn book-keeping,—an occupation for which young Laurent exhibited the greatest aversion. He preferred occupying himself with mechanical contrivances, and for some time devoted himself with ardour to the discovery of perpetual motion.

Amongst the constructions proceeding from the hands of the young scholar, was a small mill, the very ingenious mechanism of which excited the admiration of connoisseurs. His teachers, moreover, were not slow in perceiving the young man's dispositions and inclination for science; and accordingly, they obtained his father's consent to direct his attention to the higher courses of study.

His father lost no time in sending him to Paris. In 1826, young Laurent, then at the age of 19, entered the "E'cole des Mines," which he left in 1829 with the diploma of "Ingénieur des Mines." He then set out to travel in Germany; went through Austria, Poland, Saxony, and the Rhine provinces; visited the mines and factories of those countries, and returned with a rich budget of notes and observations.

Among the sciences taught at the E'cole des Mines, there was one by which young Laurent's mind was especially captivated: this science was Chemistry,—to which, accordingly, as soon as he had become a little more master of his actions, he devoted himself exclusively. He then put the last touches to some researches commenced at the E'cole des Mines, on the treatment of cobalt-ores, the preparation of smalt, cobalt-blue, &c.,—also on the treatment of arsenical ores; and entered upon Organic Chemistry. These researches were made at the "E'cole centrale des Arts et Manufactures," which he had just entered in the capacity of "Préparateur." Being soon afterwards appointed chemist at the manufactory at Sèvres, he assisted in the researches of M. Brogniart, and made a number of observations and analyses, the results of which are recorded in the "Traité des Arts céramiques" of that mineralogist. In the course of these inquiries, he invented a process for the analysis of alkaline silicates, which is still in use at the present day.

But the kind of work pursued at Sèvres agreed but ill with the direction of Laurent's mind; he had but little time to devote to his favourite studies; and preferring scanty means, and even privation, to a mode of life which did not satisfy his intense desire for independence of mind and thought, he resigned his appointment at Sèvres, and quietly located himself in a garret in the Rue St. André des Arts. He there fitted up a laboratory, which was soon frequented by pupils, all of whom remained attached to him: among them we find two persons,—M. Prat, a merchant, and the distinguished surgeon, M. Maisonneuve,—with whom he contracted friendships which lasted the end of his life.

This new position imposed other duties upon Laurent. The pains which he took with his pupils absorbed the greater part of his time,

and on the whole he did not gain much by the change; indeed, he was even less able than at Sèvres to devote himself to his researches with any degree of continuity. Having, therefore, after some time, accumulated a little money, he dismissed his pupils, and applied himself earnestly to recover the time which he had lost for the realisation of his projects,—working night and day in his laboratory, and endeavouring to make the small sum which he had saved last as long as possible. But this life, so full of enjoyment for Laurent, could not go on indefinitely; he soon found himself near the end of his savings; and he was well aware that the parsimonious life he was leading, and the privations he imposed upon himself, could not much longer avert the destitution which was already knocking at his door. He therefore reopened his laboratory for purposes of instruction; his pupils, who had not taken offence at their dismissal, returned in a body; paid regularly at the end of each month the 80 francs required for their instruction; and soon placed their master in a condition to dismiss them a second time.

This trait is peculiarly characteristic of Laurent, who was indeed the personification of the motto: "La science pour la science;"—science for its own sake, apart from all material interests. Accordingly, we shall see him lose his way, every time that he attempts to apply his knowledge to industrial purposes.

Science had indeed complete possession of his soul; to her he had devoted himself without reserve, and without foreseeing the end to which such a course would conduct him. The nature of his prevailing ideas at this time may be very exactly ascertained from a thesis which he presented to the "Faculté des Sciences" at Paris, on the 20th of November, 1837, to obtain the degree of "Docteur des Sciences."*

These high theoretical inquiries had completely detached him from earth, and when at length he began to look about him, he found himself poorer than ever. He therefore accepted an offer made to him by a perfumer, whose establishment in the Rue Bourg-Lobbé he entered in the capacity of chemist, and there passed his time in distilling essences and testing their purity. Not being much troubled with artificial wants, he never demanded any regular salary from his employer, but contented himself with occasionally receiving a five-franc piece for the supply of his most urgent necessities. In this establishment, where he continued for nearly two years, his observing spirit found ample means of satisfaction and amusement; he used to

* Théorie des Combinaisons organiques (Ann. Ch. Phys. [2], 61, 125). See the propositions at the beginning of this thesis.

take peculiar pleasure in stationing himself occasionally in the shop, and making his observations on the vanities and prejudices of the elegant and high-bred persons who frequented it.

During all this time, however, though unable to devote himself continuously to his scientific researches, he kept them steadily in view, and maintained with care the sacred fire of his soul, taking advantage of his intervals of leisure to collect his ideas and arrange them in a regular system. This was the object of the above-mentioned thesis,—in which, in fact, he developed the nucleus-theory, the theory of substitution, and, in general, the ideas which guided him in his researches. The exposition of these theories led to a lively discussion between Laurent, M. Thénard, the Dean, and M. Dumas, the Professor, of the Faculty of Sciences; and after a two hours' contest Laurent received the diploma of "Docteur en Science." This was on the 20th of November, 1837, just seven years after he had taken the degree of "Ingénieur des Mines."

After this discussion, Laurent descended, though with regret, from the high ground of theory, and returned bravely to the perfumer's laboratory to resume his daily labour. His position in this establishment was comfortable enough in a material point of view, but offered no prospect of advancement. He therefore, in the hope of enlarging his means of action, accepted an offer from the General Belgian Society, then recently founded for the purpose of establishing a porcelain manufactory in the Duchy of Luxembourg. Laurent was appointed chemist to this society, and soon afterwards set out for his post. On settling accounts with his old patron, the perfumer, he found, to his great surprise, that, during the eighteen months that he had passed there, he had gained a sum of 10,000 francs. This was the first sum of money he had ever earned by the application of his knowledge to industrial purposes, and it was also the last: we shall presently see by what strange destiny this money proved to be of no use, either to Laurent or to science.

This new position was destined to exert a powerful influence on his future career. At Luxembourg he married; and feeling the necessity of gaining a more permanent station, he accepted an appointment in the University, and repaired to Bordeaux in the capacity of Professor of the Faculty of Sciences. This was on the 30th of November, 1838. It was at Bordeaux that his most important researches were performed.

But though incessantly occupied with the furtherance of his theoretical views, he nevertheless paid some attention to industrial application. The feeling of responsibility as a father of a family, together

with the advice of his friends, having induced him to direct his ideas and knowledge towards a practical and lucrative end, he entered into partnership with a merchant for the purpose of manufacturing sulphate of magnesia and sulphate of copper. The undertaking turned out a failure; and Laurent was only too happy to regain his liberty by sacrificing the 10,000 francs which he had saved while working at the perfumery. His own account of the termination of this affair is as follows: "En apercevant la pente sur laquelle je me trouvais, je demandai à mon associé de rompre notre contrat; je lui dis: Tenez; voici toute ma fortune; elle s'élève à 10,000 francs; prenez cette somme, à la condition que je n'entende plus parler de cette malheureuse affaire, et que dès aujourd'hui je lui sois complètement étranger." From the issue of this adventure, he concluded that it is useless to attempt to quit the sphere of action which our capacities, tastes, and vocation may have assigned to us;—he found, indeed, that he had not a practical turn of mind, and from that time forth devoted himself exclusively to the theoretical part of science.

In 1844, he made an excursion into Germany, and went to Giessen, where he was most kindly received by Liebig, with whom he had for some years been engaged in controversy. Liebig begged him to give a public lecture on his views, and placed the "Annalen" at his disposal for their publication.

On the 11th of August, 1845, he was elected a Corresponding Member of the Academy of Sciences, in place of Mr. Faraday, who was made an Associate.

Bourdeaux, being an essentially literary town, offered but few scientific resources to Laurent; hence he had for some time resolved on returning to Paris,—a project which he put in execution in the beginning of the year 1846; resigning his appointment, and leaving Bordeaux with his wife and son. Being without fortune, and receiving only half his salary (2,000 fr.), he quietly took up his residence in a fourth story in the Rue de l'Université, dividing his time between his family, a few pupils, and some researches which he performed at the laboratory of the E'cole Normale,—a laboratory which M. Balard, who was then Maître de Conférence, had placed at his disposal.

Being actuated by great delicacy of feeling, Laurent was not quite at ease in a laboratory which was not his own. He was afraid of being troublesome; and in order to occasion as little expense as possible, he made choice of subjects which did not require costly materials or large and expensive apparatus. In this manner he made his researches on the tungstates, borates, silicates, double cyanides, &c.; looking

forward to the time when he might be able to get a laboratory of his own,—an expectation which was, however, but imperfectly fulfilled. On the 14th of May, 1848, he was appointed Assayer to the Mint:—an appointment which did not, however, furnish him with a laboratory; but it fixed his position, and enabled him to devote a certain sum to his researches. He set to work immediately, and installed himself in a corner of the Hôtel de la Monnaie, in a kind of cellar, dark, damp, and unhealthy, where he resumed, as far as his means would allow, his former activity of investigation. There he passed all the time that he could spare from his official duties, and there, unfortunately, he contracted the malady which afterwards consigned him to the grave.

Two years were thus passed in the laboratory,—two years well employed for science. Engaged on nearly all subjects of organic chemistry, and in analysing the most complicated mixtures, Laurent yet found the means of extending his hospitality to one or two chemists who had no laboratories, and furnishing them with the means of working. His laboratory was the rendezvous of a great number of scientific men; there was no lack of news there; and Laurent had every day some new result to announce, or some new idea to develope. Raw materials were also sent to him from all sides for examination. Among other matters of this kind, mention is made of a certain amorphous precipitate, which no one was able to recognise, prepared by a chemist who refused to state the means by which he had obtained it, and, moreover, shrank from the difficulty of obtaining anything definite from it. Laurent was totally ignorant of its origin,—but that made little difference to him. He employed his usual reagents, and in a few hours succeeded in extracting from it a beautiful yellow crystalline substance consisting of a nitro-compound of the phenyl series. The amorphous precipitate was a residue obtained by treating coal-tar naphtha with nitric acid.

Laurent possessed a degree of analytical tact never before known; his researches on napthalin, indigo, bitter-almond oil, &c., remain as monuments of a genius for investigation which, unfortunately, will not soon be equalled. The immense number of new compounds which he discovered—for which, indeed, he was obliged to create a new nomenclature—were prepared with the aid of a small number of reagents; and the merit of these researches is further increased by the consideration that they were not merely the inspiration of an active mind, but were conceived under the influence of a fundamental idea of which the substitution-theory is one of the consequences. With chlorine, nitric acid, ammonia, sulphuric acid, and potash, Laurent produced his combinations and decompositions; water, alcohol, ether,

and the goniometer, served him for the recognition and isolation of his products. He was the first to employ the goniometer as a reagent, and no one knew better how to manage it. He had learnt the use of it while pursuing his studies at the E'cole des Mines, and had early recognised its utility in purely chemical investigations. At an early period, also, he had laid down the fundamental proposition, that: "Form and arrangement may be as important as composition,"—a proposition round which all his researches may be said to gravitate. The consequences which followed from it are well known; their names are: Theory of nuclei; theory of substitution; divisibility of atoms; paramorphism; hemimorphism; isomeromorphism; multiple equivalents; law of even numbers, &c.

In the midst of these brilliant discoveries, Laurent devoted himself to his work with daily-increasing ardour, each laboratory-session yielding its contingent of new results. As if aware of the premature end which awaited him, he used all his efforts to produce and to consolidate. Happily for science, but unfortunately for his family, this preoccupation of his mind bore sway over every other consideration, and made him totally negligent of the material side of life; as a pioneer of the future, he belonged especially to humanity, and devoted himself entirely to his mission as one who thoroughly appreciated it.

This feverish existence could not last long. For some time Laurent had suffered from an affection of the chest; and the physicians, dreading the complications which afterwards showed themselves, forbade him the use of his laboratory. Being thus prevented from pursuing his experimental labours, he devoted himself more especially to critical inquiries. His friends, with MM. Biot and Balard at the head, took advantage of this circumstance to suggest to him the idea of collecting his ideas and theories in the form of a systematic work. We have already seen that Liebig made a similar proposal to him in 1844, but Laurent, not thinking his theory to be then sufficiently matured, did not avail himself of the opportunity;—in fact, he saw too many voids in organic chemistry to be disposed to hazard a definite theory. However, the materials for the work were now prepared; for Laurent had been for many years in the habit of carefully registering the new facts of chemical science as they came out. These records were of the greatest utility in the compilation of his book, and by their aid he was enabled, in a comparatively short space of time, to compose a colossal work, the full scope of which will be seen when the tables which he has annexed to the treatise at present going through the press, are published.

This book supplied him with constant occupation; as long as he was able to hold a pen, he worked at it with a degree of vigour and activity which excited the admiration of those who were acquainted with his situation. Laurent, indeed, had never deceived himself about the fate which awaited him; it was not the mere prospect of death which alarmed him, but he was about to leave a wife and two children in a state of destitution; he had had no time to amass wealth, nor had he rendered a sufficient amount of administrative services to hope for a pension for his widow. These harassing thoughts were not of a nature to ameliorate his already hopeless state; and those who approached his bedside during his intervals of delirium could well appreciate the poignant grief which oppressed the dying man.

His delirium, however, was only occasional, and he retained his reason to the last moment. At times, indeed, he entertained hopes of improvement, and then began to think of resuming some investigation, verifying some fact, or examining some opinion: then, as throughout his life, ideas flowed rapidly in his brain; but he breathed painfully, and could not speak without the greatest difficulty. It might then be observed that he endeavoured to include the greatest possible meaning in the fewest words; but his sufferings increased, his respiration became more and more laborious, and he was even denied the consolation of making known his dying thoughts.

Laurent was of a very kind and obliging disposition; extremely indulgent to others; and his friendship was capable of standing the severest tests. To a just sentiment of his own dignity, he united great firmness in his convictions; his mind revolted from injustice; and he was always ready to acknowledge his errors, and even to go over to the side of his adversary, as shown especially in his discussion with Gerhardt, in 1844, on the constitution of draconic acid, &c.* He was one of those persons of whom it may be said that they improve upon acquaintance. Cold and reserved at first, he soon became confiding and expansive, and removed any unfavourable opinion that might have been formed of him from hearsay. He may have been envied, but he had no enemies; he sometimes met with ingratitude, even from those on whom he had conferred the greatest benefits:—such ingratitude, in fact, embittered his last moments. Possessed of great sensibility, he felt keenly any wound inflicted on his self-love, and suffered more than most persons when he found himself misunderstood. With this character was joined a defect not very well calculated to diminish the annoyance which he suffered from such

* Vide "Liebig et la Chimie."

causes;—like Jean-Jacques Rousseau, he fancied he had more enemies than he really had.

The Council would have been glad to have had it in their power to report something positive to the Fellows on a subject of much interest to this as well as to other Scientific Societies in this Metropolis; viz. their juxtaposition in some central position, under one roof, and free of cost. Although the Council cannot state that any material progress has been made in the settlement of this question, which the disturbed aspect of public affairs has probably assisted to keep somewhat in abeyance, yet, from all the Council have been able to learn, there is good reason to hope that the object will be eventually attained, and a building allotted in a situation which will satisfy the wants of the different Societies.

The following is a list of the papers read before the Chemical Society, from March 30, 1853, to March 30, 1854.

1. "On some Compounds of Urea, and on a New Method for the Determination of Chloride of Sodium and of Urea in Urine:" by Baron Liebig.
2. "On the General Distribution of Iodine and Bromine:" by Stevenson Macadam.
3. "On the Solid Compound obtained by Distilling Stearic Acid with Lime:" by Thomas H. Rowney, Ph.D.
4. "On Deposits of Soluble or Gelatinous Silica in the Lower Beds of the Chalk Formation:" by John Thomas Way.
5. "On a Compound Sulphate of Potash and Soda:" by J. H. Gladstone, Ph.D.
6. "Note on Thierschite:" by Baron Liebig.
7. "On Kianurenic Acid:" by Baron Liebig.
8. "Analysis of the Waters from the Deep Well of the Westbourne Waterworks at Westbourne Grove, the Well in Russell Square, and the Artesian Well at the Hanwell Lunatic Asylum:" by C. Harwood Clarke, M.A. and Henry Medlock.
9. "On the Increase of Weight in Molasses Casks which occasionally arises from Endosmose:" by William Ferguson.
10. "On some New Basic Products obtained from Vegetable Alkaloids:" by Henry How.
11. "On the Conditioning of Silk:" by P. J. Chabot, M.A.
12. "On a New Method of Estimating the Strength of Chloride of Lime:" by Astley P. Price, Ph.D.
13. "On a Gas Furnace for Organic Analysis:" by Dr. Hofmann.

14. "On the Constitution of Salts considered as Substitution-products formed on the Type of Water:" by Dr. Odling.

15. "On New Methods for the Determination of Nitrogen in Organic and Inorganic Compounds:" by Dr. Maxwell Simpson.

16. "On Ethers intermediate between the Œnanthylic and the Ethylic, Methylic, and the Amylic Series:" by A. W. Wills.

17. "Analysis of the Ash of Lemon Juice:" by Henry M. Witt.

18. "On the Platino-tersulphocyanides and the Platino-bisulphocyanides, two new Series of Salts, and their Decompositions:" by George Bowdler Buckton, F.L.S.

19. "Note on the Valuation of Protochloride of Tin:" by Dr. Penny.

20. "Note on Platinum accompanying Silver in Solution in Nitric Acid:" by Henry How.

21. "On the so-called Iodide and Chloride of Nitrogen:" by J. H. Gladstone, Ph.D.

22. "On some New Compounds of Salicyl:" by Charles Gerhardt.

23. "On Red Prussiate of Potash:" by William Wallace.

24. "On the Existence of Trimethylamine in the Brine of Salted Herrings:" by G. H. Winkles.

25. "On the Action of Iodide of Ethyl on Toluidine:" by Reginald J. Morley and John Abel.

26. "Critical Observations on Williamson's Theory of Water, Ethers, and Acids:" by H. Kolbe.

27. "Reply to the foregoing Paper:" by Dr. Williamson.

If, with the view of ascertaining to what branch of chemical science the labours of this Society have most contributed during the past year, we attempt to classify these papers according to the method adopted in Liebig's Annual Report, we find ten are devoted to general and inorganic chemistry, seven to organic chemistry, six to analytical processes and apparatus, two to technical, one to mineralogical, and one to geological chemistry.

In order to meet the feelings of many Fellows of the Society, to the effect that it was desirable to introduce into our meetings a little more life and general interest than could be elicited by the reading of the original communications addressed to the Society, the Council passed the following Resolution in June last:—

"In order to increase the interest of the Meetings of the Society, certain Meetings, not exceeding five in the year, shall, after the

transaction of the ordinary business of the Society, be devoted to the delivery of discourses on matters connected with the progress of Chemistry, and which may be illustrated by experiment.

"It is not proposed that these discourses shall be published in the Journal; but where new matter, either theoretical or experimental, is contained in them, such matter may, with the consent of the Council, be published in the form of an abstract or paper.

"It is proposed that after the discourse discussion shall be invited, and in cases in which the matter of the discourse is published in the Journal, explanations and remarks upon it, offered in discussion, may, with the consent of the Council, be appended."

This Resolution has as yet been carried into effect in one instance only, when the Society was indebted to Professor Graham for an able and elaborate discourse on "the Liquid Condition of Matter." This was followed by an interesting discussion, in which several eminent Fellows of the Society took a part. Judging, then, from the result of this trial, the Council are justified in anticipating that the plan will realize their hopes; but the Council are desirous of impressing on the Fellows their opinion that the character and position of the Society must mainly depend on the value of the original communications which may be published in the Journal of the Society.

It will no doubt be a matter of interest to the Fellows of this as well as of other Societies cultivating physical science, to learn that the Royal Society purposes an important alteration in the manner and nature of the publication of their Proceedings.

The Royal Society proposes to publish these Proceedings once a month during the session; to send them free to all Fellows, and to other persons on the payment of an annual subscription of five shillings; and they propose, in addition to the matter heretofore published in the Proceedings, to give, among other things, readable abstracts of papers which are to be, or which have been presented to other Societies, but not yet read, when communicated as usual through Fellows of the Royal Society.

The design of the Royal Society includes some other particulars; and if carried out, it will render the Proceedings of the Royal Society the *compte-rendu* of all the work done in physical and natural science throughout the country.

Dr. ROBERT PORRETT (TREASURER) IN ACCOUNT WITH THE CHEMICAL SOCIETY OF LONDON. *Cr.*

1853.		£	s.	d.
March 26.	To Balance from last Account	122	18	6½
1854.				
March 27.	„ Subscriptions, £275 2s. and Compositions, £20, since received	295	2	0
„ „	„ Admission Fees from ten new Members	20	2	0
„ „	„ One Year's Dividend on £300 3 per Cent. Consols, minus Property Tax	8	14	10
„ „	„ Proceeds of Sale of "Memoirs"	5	11	5
	„ Three Quarters of a Year's Rent for the use of the Rooms to Christmas last, from the Microscopical Society	15	0	0
	£	467	8	9½

1854.		£	s.	d.
March 27.	By Payment to Directors of Polytechnic Institution for One Year's Rent to 25th inst.	120	0	0
„ „	„ Ditto to Henry Watts for One Year's Salary as Editor of the Society's Journal	50	0	0
„ „	„ Ditto to H. Baillière for publishing the Society's Journal	109	11	0
„ „	„ Ditto to John Kirkman for Attendance, and for Tea and Coffee	33	2	0
„ „	„ Ditto to Dr. Hofmann for Translations by S. Abel and H. Bottinger	5	8	6
„ „	„ Ditto for Petty Cash, Postage Stamps, &c.	6	9	4
„ „	„ Ditto to Imperial Gas Company for Gas	1	5	0
„ „	„ Ditto to Cavendish Society Subscription, 1854	1	1	0
„ „	„ Ditto to H. Baillière for Books	7	16	0
„ „	„ Ditto to David Nutt for Books	0	16	0
„ „	„ Ditto to Taylor and Francis for Philosophical Magazine, &c.	4	11	6
„ „	„ Ditto to Thomas Reed for Account Books and Paper	3	2	0
„ „	„ Ditto to Charles Whiting for Printing	4	15	0
„ „	„ Ditto to George Green for Carpenter's Work	1	8	0
„ „	„ Ditto to the Collector for Poundage	13	0	7
„ „	„ Balance carried to next Account	105	2	10½
	£	467	8	9½

London: 27th March, 1854.

R. PORRETT, Treasurer.

Examined and found correct.
G. B. BUCKTON.
WILLIAM FERGUSON.

NOTICES

OF

PAPERS CONTAINED IN OTHER JOURNALS.

By Henry Watts, B.A., F.C.S.

Chemical Analysis of the Mineral Waters of Harrogate.

By A. W. Hofmann.

REPORT ADDRESSED TO THE CHAIRMAN OF THE WATER COMMITTEE IN HARROGATE.

Of the mineral springs which abound in the neighbourhood of Harrogate, the following ten were selected for examination, representing the principal varieties occurring in that locality.

A. SULPHUR WATERS.

1. Old Sulphur Well.
2. Montpellier Strong Sulphur Well.
3. Montpellier Mild Sulphur Well.
4. Hospital Strong Sulphur Spring.
5. Hospital Mild Sulphur Spring.
6. Starbeck Sulphur Spa.

B. CHALYBEATE WATERS.

1. Montpellier Saline Chalybeate.
2. Cheltenham Saline Chalybeate.
3. Tewitt's Well.
4. St. John's Well.

The waters used for the estimation of the solid constituents were collected during the months of May 1853 and 1854; the gases, partly in November 1853, partly in February 1854.

Qualitative analysis, performed in the usual manner, exhibited the presence of the following substances:—

BASES.	ACIDS, OR ELEMENTS REPLACING THEM.
Potassa	Chlorine
Soda	Bromine
Lime	Iodine
Magnesia	Fluorine
Protoxide of iron	Sulphur
Protoxide of manganese	Sulphuric acid
Alumina	Carbonic acid
Ammonia	Silicic acid

Organic matter.

GASES DISSOLVED IN THE WATERS, OR RISING IN BUBBLES FROM THE WATERS.

Oxygen
Nitrogen
Carbonic acid
Carbonetted hydrogen (marsh gas)
Sulphuretted hydrogen

These are, with the exception of fluorine and manganese, the same constituents, the existence of which, in the Harrogate waters, has been pointed out by Mr. West. Iodine and bromine have been traced by the same chemist in the Old Sulphur Well; these elements are, however, present in nearly all the waters.

If the above-mentioned constituents be arranged according to the solubility of their compounds either in pure water, or in water containing free carbonic acid in solution, it may be assumed that the Harrogate waters contain

a. COMPOUNDS SOLUBLE IN WATER.	*b.* COMPOUNDS SOLUBLE IN WATER CONTAINING FREE CARBONIC ACID.
Sulphate of lime	Carbonate of lime
Fluoride of calcium	Carbonate of magnesia
Chloride of calcium	Carbonate of iron
Chloride of magnesium	Carbonate of manganese
Chloride of potassium	Alumina.
Chloride of sodium	
Sulphide of sodium	
Iodide of sodium	
Bromide of sodium	
Carbonate of soda	
Carbonate of potassa	
Silica	
Ammonia.	

The method of quantitative analysis which was followed, requires scarcely any special notice, since it differed in no essential point from that usually adopted for this purpose. Chlorine and sulphuric acid were determined in separate quantities of the water by means of nitrate of silver and chloride of barium; lime and magnesia together in the same portion of water respectively by oxalate of ammonia, and ammonio-phosphate of soda. The silica was estimated by evaporating a separate portion, and treating the residue with hydrochloric acid; the alkalies, by precipitating iron, lime, and magnesia, by baryta-water, repeatedly evaporating to dryness in order to remove small quantities of baryta from the solution, and weighing the mixed chlorides; the separation of the alkalies was effected in most cases by bichloride of platinum, in some cases their relative proportion was determined by the indirect process. The iron had been partly deposited from some of the waters by the time they arrived in London; it was, therefore, precipitated in a special experiment at the

well by means of sulphide of ammonium from pretty large quantities of the waters, and ultimately weighed as sesquioxide. Lastly, the total amount of solid residue was obtained by evaporating the water, to which a weighed quantity of carbonate of soda had been added, and carefully drying at a temperature of from 248° to 266° F. (120° to 130° C.); exposure of this residue to a low red heat in contact with the air gave the amount of organic matter.

Bromine and Iodine.—Bromide and iodide of sodium, although present in quantities so small as to be incapable of being quantitatively determined with accuracy, were easily *detected* in most of the waters: from 1000 to 1500 grains of the solid residue obtained on evaporation were exhausted with water, the solution evaporated, and the residue boiled out with spirits of wine; the extract left on evaporation was again exhausted with stronger alcohol. In the residue left on evaporating this extract, both bromine and iodine were generally traced without any difficulty; in some cases, however, the treatment with alcohol had to be repeated. The bromine was detected by dissolving the residue, left on distilling off the alcohol, in a small quantity of water, decomposing the bromide by chlorine-water, and taking up the liberated bromine in a small quantity of ether, with which the liquid was agitated: the yellow colour which the ether assumed indicated the bromine. In order to trace the iodine, a portion of the same residue was dissolved in a small quantity of water, mixed with starch paste, and evaporated to dryness in a porcelain capsule, at a gentle heat; on adding a drop of concentrated nitric acid to the mixture, the blue colour of the compound of starch and iodine made its appearance; in the presence of a bromide, the starch, where it came in contact with the *liquid* nitric acid, assumed a deep orange-yellow colour, and the colour of the iodine-compound appeared distinctly in those parts of the saline residue which were exposed only to the *vapour* of the bromine and the nitric acid: in this manner both elements could be readily detected in the same experiment.

The quantities of bromine and iodine appear to vary in the several waters, but I am unable to make a positive statement as to this fact, inasmuch as the different quantities of saline residue left on the evaporation of equal amounts of water compelled me to use very unequal portions for the purpose of testing for bromine and iodine. The quantities of saline residue actually employed were 1500 grains in the case of the Old Sulphur Well, the Hospital Strong Sulphur Spring, the Montpellier Saline Chalybeate, and the Cheltenham Saline Chalybeate Wells; 750 grains of that of the Montpellier Mild Sulphur Well; and 500 grains in the case of the Montpellier Strong Sulphur Well, the Hospital Mild Sulphur Spring, and the Starbeck Sulphur Spa; and lastly, 100 grains of the Tewitt's Well residue.

Fluorine.—The fluorine had to be sought for in the insoluble portion of the saline residue of the waters. This residue was tested by Dr.

G. Wilson's excellent process. From 400 to 600 grains of the residue, consisting chiefly of calcareous and magnesian salts, were mixed with a small quantity of pure finely-divided quartz, and boiled for about an hour with concentrated sulphuric acid. The terfluoride of silicium disengaged in this manner was passed into water, the resulting hydrofluosilicic acid decomposed by ammonia, and the fluoride of ammonium, after separation of the silica by filtration, evaporated; gently heated with concentrated sulphuric acid in a platinum crucible, this residue disengaged hydrofluoric acid, which was recognised by its action upon glass. In the examination of several of the waters which had deposited rather a large quantity of insoluble matter, the presence of fluorine became at once perceptible on passing into water the gas evolved by boiling, with concentrated sulphuric acid, a mixture of the residue and quartz: a flocculent precipitate of silica was thrown down, which was considerably augmented on addition of ammonia. In those cases the etching was very rapidly effected, and to a considerable depth; in other cases, however, the separation of silica was scarcely perceptible, and the etching very faint. In some cases the etched lines became visible only in the film of moisture produced by breathing upon the glass plates. In none of the waters was found a sufficient amount of fluorine to admit of quantitative estimation.

Manganese.—Of all the methods suggested for the detection of small quantities of manganese, none yields more accurate results than the one discovered some years ago by Mr. Walter Crum. It consists in treating the iron precipitate which may contain the manganese with nitric acid, and adding a small quantity of binoxide of lead. If manganese be present, the liquid exhibits, as soon as the precipitate has subsided, the magnificent colour of permanganic acid. By applying this method to the insoluble portion of the saline residue, the presence of manganese in the Harrogate waters could be proved without difficulty, but the amount was not sufficient for quantitative determination.

Ammonia, which could be detected in all the waters, if considerable quantities were evaporated, with a few drops of hydrochloric acid on mixing the residue with recently-slaked lime, was likewise present in such a minute proportion that quantitative determination became impossible.

Alumina was detected only in one case by means of the blow-pipe reaction with nitrate of cobalt, after separation of silica and iron, and in this case not more than a mere trace was found.

All the waters were very carefully examined for *arsenic, antimony,* and *tin,* which have been found of late in so many mineral springs. But although large quantities of the solid residue obtained by evaporation were submitted to analysis, no trace of these metals could be detected.

Not more successful was the attempt to trace the presence of *nitric* and *phosphoric acids,* or of *lithia* and *strontia,* in the Harrogate waters.

The *nitric acid* was tested for by means of sulphuric acid and sulphate of iron in the residue of a large quantity of water, evaporated with a few grains of carbonate of soda. *Phosphoric acid* had to be looked for both in the soluble and insoluble part of the solid residue obtained by evaporating the water. Both were carefully tested by means of molybdate of ammonia, the insoluble portion after the removal of the iron.

In order to find *lithia*, the solid residue of the waters (the experiment was made with the following three waters, viz.: the Old Sulphur Well, the Hospital Strong Sulphur Spring, and the Cheltenham Saline Chalybeate) was repeatedly boiled out with water, the solution neutralised with a few drops of hydrochloric acid, evaporated to dryness, and the residue exhausted with alcohol. The saline residue obtained by distilling off the alcohol was then treated with a mixture of alcohol and ether. The solution thus formed neither exhibited the crimson-red lithia-flame when lighted, nor was it possible to obtain from it the difficultly-soluble double salt of phosphate of soda and lithia.

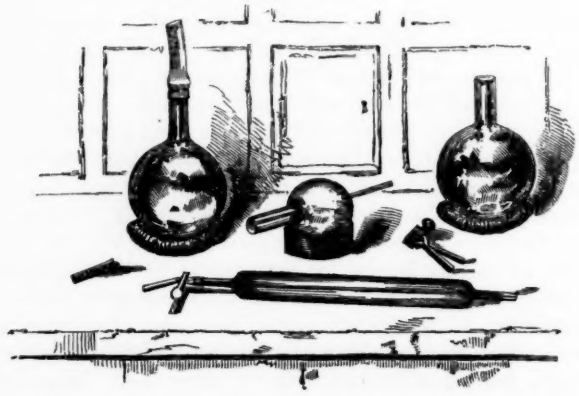
Strontia, when existing in the waters, was probably present in the form of sulphate, and had therefore to be sought for principally in the insoluble portion of the saline residue. According to recent observations, however, sulphate of strontia is slightly soluble in water containing a considerable quantity of chlorides. In order, therefore, not to lose any strontia, the whole saline residue was submitted to the action of sulphuric acid, the excess of this acid expelled by ignition, and the residue of sulphates exhausted first by water and then by hydrochloric acid. The residue, consisting chiefly of silica, was fused with carbonate of soda, the product of the fusion exhausted with water, and the insoluble residue which was left, dissolved in hydrochloric acid. Addition of sulphate of lime to this solution, produced the faintest turbidity, which may have been occasioned by strontia. But unless the experiment be repeated on a very large scale, it would be hazardous to assert the presence of strontia. The experiment was made with the residue of the Old Sulphur Well, which contains a very large amount of saline matter.

In collecting and analysing the *Gases* contained in the Harrogate waters, I have availed myself of the processes invented by Professor Bunsen, and so remarkably perfected within the last few years by his admirable researches. Since these processes, especially those of collecting the gases, differ from the methods formerly adopted for this purpose, and since any accurate information regarding the nature of the gases, however precise our methods of analysis may be, depends, in the first place, on the means we employ for collecting and measuring their total amount, I will briefly describe here the principal features of Bunsen's process, which consists in expelling the gases by ebullition *in vacuo*.

For this purpose a globular glass flask, over the neck of which is fitted a strong vulcanised caoutchouc tube, (*see* Fig. 1), is immersed in the water until it is filled, and the tube is then closed by means of a brass screw-clamp, which is screwed immediately above the neck of the flask.

In this manner a quantity of water is secured which has not been in contact with the air, and the exact volume of which may be readily

Fig. 1.

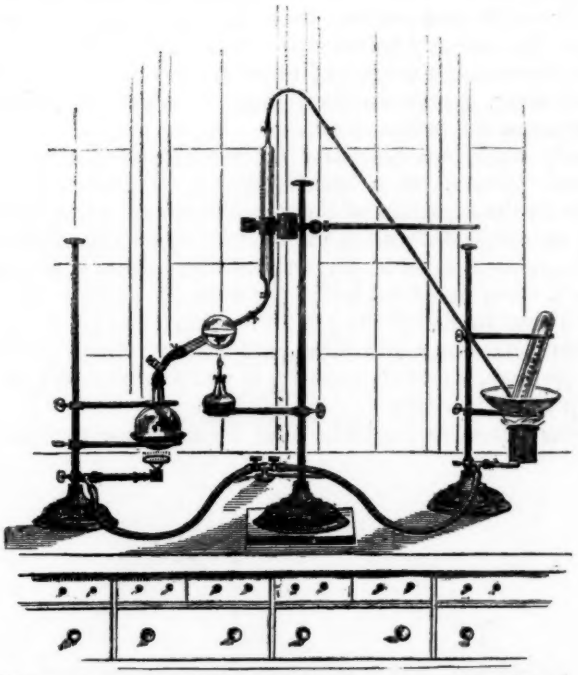


determined by experiment. The caoutchouc tube is then connected with a small glass globe partially filled with water, and provided with two necks opposite each other, the one corresponding in diameter to the neck of the flask, the other of the size of an ordinary quill pen. By the latter, the globular vessel, which for the sake of shortness I will call the "boiler-globe," may be connected with a glass tube about 10 inches long, and $\frac{3}{4}$ of an inch wide, and terminating on each side in a narrow open connecting tube, corresponding in width to the narrow tube of the boiler-globe. The connection of the latter and the tube, which may be termed the "gas receiver," is effected by means of a caoutchouc tube just sufficiently long to admit between the two glass tubes, which are fixed into its ends, the application of a small brass screw-clamp, by means of which arrangement communication between the two vessels may be established or interrupted. In a perfectly similar manner, the other extremity of the gas-receiver is connected with an ordinary delivery tube which discharges into water.

Fig. 2 represents the apparatus fitted up, and fixed upon an ordinary gas-stand. The water-flask is closed with a screw-clamp, but the communication between the boiler-globe, gas-receiver, and delivery-tube, is perfectly free. The water in the boiler-globe is heated to ebullition by means of a spirit-lamp, and kept boiling for about a quarter of an hour, by which time all the air in the apparatus is perfectly replaced by steam, which may be ascertained, moreover, by

not a trace of air collecting if the delivery-tube be made to discharge for a few minutes under an inverted bell-jar, filled with water. The caoutchouc tube, at the upper end of the gas-receiver, is now closed by a brass clamp, and the spirit-lamp simultaneously removed, when

Fig. 2.



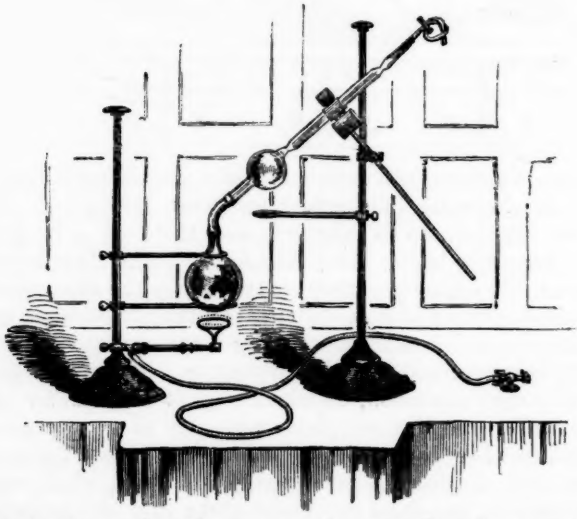
the ebullition *in vacuo* will continue for a considerable time. The boiling-out of the water in the flask may now commence. For this purpose the brass clamp is removed, and the flask submitted to a gradually increasing heat. Air-bubbles soon make their appearance, but a quarter of an hour generally elapses before the caoutchouc tube, which is collapsed and almost flattened by the atmospheric pressure, is sufficiently expanded to admit of a free communication between the flask and the upper part of the apparatus. The water gradually enters into violent ebullition, in which state it is kept for about an hour, so as to ensure the complete expulsion of every trace of gas. When this point has been reached, the heat is increased for a moment, and a good deal of steam is generated in the flask, which causes the water gradually to rise from the boiler-globe into the narrow end of the gas-receiver. At this moment, the flask is closed with the clamp, and the source of heat removed; the water in the boiler-globe begins to cool, gradually contracts, and descends in the narrow tube of the gas-

receiver; the very moment its level disappears under the caoutchouc connector, the clamp between the boiler-globe and gas-receiver is fastened, and the whole apparatus disconnected. The gas-receiver closed at both its extremities by caoutchouc contains the whole of the gas, together with a few drops of water: the volume of the gas may be readily measured by opening one of the clamps under mercury, and allowing the metal to enter the gas-receiver, until it stands at the same level within and without the tube; the clamp is then secured again, and the mercury transferred into a graduated cylinder. The difference between the volume of mercury, and the known capacity of the gas-receiver, represents the volume of gas at the existing barometric pressure and temperature.

The only conditions necessary for the success of this apparently complicated process, are a sufficiently long ebullition, and a proper proportion in the capacities of the water-flask and gas-receiver, which can only be attained by a few preliminary operations. The capacity of the gas-receiver must be greater than the volume of the gas in the water-flask, when measured under the ordinary pressure of the atmosphere. If the volume of the gas were greater, the gas-receiver or the caoutchouc connector might burst, and if they actually withstood the outward pressure, a certain quantity of gas would be lost on opening the clamp under mercury.

The same apparatus might be used for collecting the gas intended

Fig. 3.



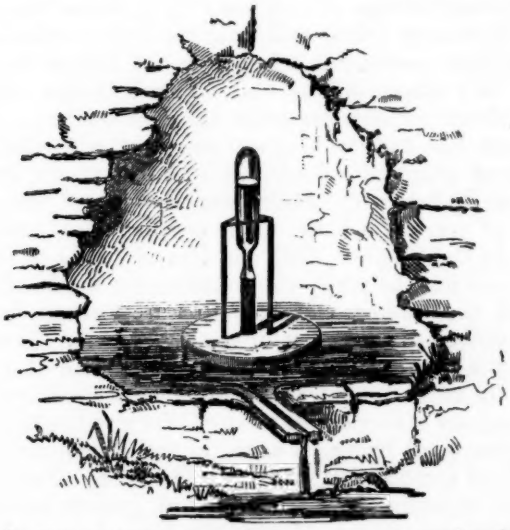
for analysis; but unless the gas can be transferred at once into the eudiometer, it is better to construct the boiler-globe and gas-receiver of one piece of glass, and to have the ends of the receiver so far

drawn out that they may be sealed by means of a blow-pipe jet. This tube, in the moment before sealing it, is represented in Fig. 3, which requires no further explanation.

The above process furnishes the gases which are dissolved in the water. The gases, however, which rise in bubbles from several of the waters, were collected in a small glass receiver constricted at one point to facilitate the subsequent sealing. This receiver is supported by an iron tripod, and fixed by means of a strong caoutchouc connector into a large perforated wooden float, the lower surface of which is hollowed out so as to collect the gas-bubbles, and cause them to ascend into the receiver, which is filled with water at the commencement of the operation. As soon as the receiver is filled, the caoutchouc connector is closed by means of a screw-clamp, the receiver disconnected and sealed before the blow-pipe.

Qualitative analysis, as has been stated, showed the gases to consist of oxygen, nitrogen, carbonic acid, light carbonetted hydrogen (marsh gas), and in several cases of sulphuretted hydrogen. Besides

Fig. 4.



these gases, in one or two cases minute traces of another hydrocarbon were observed, the presence of which was indicated by the peculiar smell of the gas.

The analysis was performed in the Volta-eudiometer, graduated and calibrated according to Bunsen's method.

After the removal of carbonic and hydrosulphuric acids by means of potash-balls, the carbonetted hydrogen was exploded with a known volume of oxygen, and estimated from the volume of carbonic acid produced after explosion. The subsequent explosion, with a known

volume of hydrogen, of the residue, freed from carbonic acid by means of a potash-ball, showed the presence and indicated the quantity of oxygen. The nitrogen was determined by difference.

The amount of sulphuretted hydrogen in the gases was determined by a graduated solution of iodine in iodide of potassium, added from a burette to a solution of the potash-ball (which had served for the absorption of this gas and of the carbonic acid) in water acidulated with acetic acid.

The total quantity of sulphuretted hydrogen which is present in the gas is never obtained by ebullition; for, in the first place, a certain quantity is destroyed by the air which is in contact with the water; and secondly, because a certain quantity is present in the form of sulphide of sodium which is but imperfectly decomposed by the ebullition of the water. On this account, the total amount of sulphuretted hydrogen was also separately determined at the well, by means of the graduated solution of iodine in iodide of potassium which has been already mentioned. This method, originally proposed by Dupasquier, and lately improved and expanded by Bunsen, is equally remarkable for its precision, and the rapidity of its execution.

All the determinations of sulphuretted hydrogen were made in the middle of February, 1854, and I mention this particularly since the amount of this compound appears to be subject to considerable variation. My attention was first directed to this subject by Dr. Bennett, whose valuable researches leave no doubt in this respect.* Dr. Bennett has had the kindness to repeat, with the same burette and the same standard solution which I had myself employed, the sulphuretted hydrogen determinations in some of the waters, after the lapse of several months, when considerable variations became manifest (see Old Sulphur Well, and Hospital Mild Sulphur Spring). These changes may be partly due to influences which affect the strata from which these waters emanate; to a great extent, however, they must be ascribed to the action of the atmosphere. It is well known how readily sulphuretted hydrogen is oxidised, and that the greatest care must be taken to protect the sulphur waters from contact with the air, especially if they are to be stored for any length of time.

The sulphuretted hydrogen exists in the Harrogate waters, partly free, partly in combination with metallic oxides. Only a portion can be expelled by boiling. We have not at present sufficient data to calculate with any degree of certainty the amount of sulphuretted hydrogen which is free, and that which is combined; and I have, therefore, introduced into the report the whole quantity in the form of sulphide of sodium, the total amount of sulphuretted hydrogen gas being moreover expressed in cubic inches.

The following Tables exhibit the results of the analyses, synoptically arranged:—

* Report on the Sulphur Springs of Harrogate, for the years 1841 and 1842. London, 1843.

A. SULPHUR WATERS.

	I. Old Sulphur Well.	II. Montpellier Strong Sulphur Well.	III. Montpellier Mild Sulphur Well.	IV. Hospital Strong Sulphur Spring.	V. Hospital Mild Sulphur Spring.	VI. Starbeck Sulphur Spa.
Temperature of air	50° F. (10° C.)	44·6° F. (7° C.)	41° F. (5° C.)	35·6° F. (2° C.)	45·5° F. (7·5° C.)	47·3° F. (8·5° C.)
Temperature of water	48·2° F. (9° C.)	46·4° F. (8° C.)	42·8° F. (6° C.)	41·9° F. (5·5° C.)	44·6° F. (7° C.)	48·2° F. (9° C.)
Specific gravity	1·01113	1·01045	1·00314	1·00515	1·0026	1·0018
Reaction	powerfully alkaline	alkaline	alkaline	powerfully alkaline	alkaline	alkaline

DIRECT RESULTS OF ANALYSIS, CALCULATED IN 1000 GRAINS.

α. Bases.	Expt.	I. Old Sulphur Well.	II. Montpellier Strong Sulphur Well	III. Montpellier Mild Sulphur Well.	IV. Hospital Strong Sulphur Spring.	V. Hospital Mild Sulphur Spring.	VI. Starbeck Sulphur Spa.
Sesquioxide of Iron	I.	trace	trace	trace	0·0166	trace	trace
	II.	—	—	—	0·0251	—	—
	Mean	—	—	—	0·0208	—	—
Manganese	I.	trace	trace	trace	trace	trace	trace
	II.	—	—	—	—	—	—
	Mean	—	—	—	—	—	—
Lime	I.	0·6816	0 6342	0·2358	0·23713	0·165	0·0632
	II.	0·6816	0·6388	0·2323	0·23037	0·164	0·0582
	Mean	0·6816	0·6366	0·2340	0·23375	0·1645	0·0607
Magnesia	I.	0·3321	0·3275	0·1239	0·11327	0·0722	0·0389
	II.	0·3304	0·3273	0·1262	0·10424	0·0722	0·0367
	Mean	0·33125	0·3274	0·1250	0·10864	0·0722	0·0376

DIRECT RESULTS OF ANALYSIS, CALCULATED IN 1000 GRAINS.—(*continued.*)

a. Bases.	Expt.	I. Old Sulphur Well.	II. Montpellier Strong Sulphur Well	III. Montpellier Mild Sulphur Well.	IV. Hospital Strong Sulphur Spring.	V. Hospital Mild Sulphur Spring.	VI. Starbeck Sulphur Spa.
Alkaline chlorides . .	I.	13·4862	11·7403	3·4357	5·5406	3 5048	1·997
	II.	13·4807	11·7462	3·4424	5·5629	3·5040	1·9954
	Mean	13·4831	11·7432	3·4390	5·5517	3·5044	1·9962
Potassa	I	0·4844	0·0521	0·0367	0·096	0·2041	0·1299
	II.	0 4749	0·0510	0·0346	—	0·2441	0·1074
	Mean	0·4795	0·0515	0·0356	0·096	0·2241	0·1186
Soda	I.	6·6587	6·1805	0·1789	2·773	1·6684	0·9903
	II.	6·7367	6·1775	0·1795	2·947	—	0·9669
	Mean	6·6977	6·1790	0·1792	2·860	1·6684	0·9786
Ammonia	I.	trace	trace	trace	trace	trace	trace
	II.	—	—	—	—	—	—
	Mean	—	—	—	—	—	—
β. Acids, or Elements replacing them.							
Sulphuric acid . . .	I.	0·0011	0·0055	0·1013	0·0429	0·0116	0·00736
	II.	0 0019	0·0044	0·1013	0·0431	0·0105	0 00727
	Mean	0·0015	0·0049	0·1013	0·0430	0·01105	0·0073
Sulphuretted hydrogen	I.	0·0961	0·0899	0·0209	0·0446	0·0166	0·0086
	II.	0·0948	—	0·0213	0·0432	0·0133	0·0083
	Mean	0·0954	0·0899	0·0211	0·0439	0 0149	0·00845

	I.	9·1900	8 0584	2·2193	3·3859	2·0797	1·0511

Chlorine	I.	9·1900	8·0584	2·2193	3·3859	2·0797	1·0511
	II.	9·1878	8·0691	2·2179	3·3713	2·0797	1·0560
	Mean	9·1889	8·0637	2·2186	3·3786	2·0797	1·054
Bromine	I.	marked trace	marked trace	very distinct tra.	marked trace	marked trace	trace
	II.	—	—	—	—	—	—
	Mean	—	—	—	—	—	—
Iodine	I.	marked trace	marked trace	very distinct tra.	marked trace	marked trace	trace
	II.	—	—	—	—	—	—
	Mean	—	—	—	—	—	—
Fluorine	I.	distinct trace	trace	distinct trace	distinct trace	trace	faint trace
	II.	—	—	—	—	—	—
	Mean	—	—	—	—	—	—
Silica	I.	0·0043	0·0261	0·0016	0·0075	0·0166	0·0215
	II.	0·0026	0·0262	0·0032	0·0076	0·0250	0 0285
	Mean	0·0034	0·0261	0·0024	0·00755	0·0212	0·0250
Total Solid Contents.							
Mineral Residue	I.	15·4754	13·5622	4·1025	6·2259	3·8593	2·239
	II.	15·4816	13·5541	4·1034	—	3·9277	—
	Mean	15·4780	13·5581	4·1029	6·2259	3·8935	2·239
Organic Matter	I.	trace	trace	trace	0·018	trace	0·0248
	II.	—	—	—	—	—	—
	Mean	—	—	—	0·018	—	0·0248
Total Residue	I.	15·4754	13·5622	4·1025	6·2439	3·8593	2·264
	II.	15·4816	13·5541	4·1034	—	3·9277	—
	Mean	15·4780	13·5581	4·1029	6·2439	3·8935	2·264

GRAINS OF SALINE CONSTITUENTS IN 1000 GRAINS OF WATER.

	I. Old Sulphur Well.	II. Montpellier Strong Sulphur Well.	III. Montpellier Mild Sulphur Well.	IV. Hospital Strong Sulphur Spring.	V. Hospital Mild Sulphur Spring.	VI. Starbeck Sulphur Spa.
Sulphate of lime .	0·0258	0·0084	0·1723	0·0734	0·0173	0·0123
Carbonate of lime .	0·1747	0·3419	0·2913	0 3630	0·2820	0·0992
Fluoride of calcium	trace	trace	trace	trace	trace	faint trace
Chloride of calcium	1·1548	0·8753	—	—	—	—
Chloride of magnesium.	0·7866	0·7729	0·2447	0·1648	0·0048	
Carbonate of magnesia	—	—	0·0463	0·0824	0·1469	0·0768
Chloride of potassium	0·9141	0·0813	0·0566	0·1527	0·3557	
Carbonate of potassa	—	—	—	—	—	0·1740
Chloride of sodium	12·2378	11·3542	3·3098	5·2446	3·1435	1·7368
Bromide of sodium	trace	trace	trace	trace	trace	trace
Iodide of sodium .	trace	trace	trace	trace	trace	trace
Sulphide of sodium	0·2187	0·2038	0·0484	0·1017	0·0043	0·0244
Carbonate of soda .	—	—	—	—	—	0·0732
Ammonia. . . .	trace	trace	trace	trace	trace	trace
Carbonate of iron .	trace	trace	trace	·0150	trace	trace
Carbonate of manganese	trace	trace	trace	trace	trace	trace
Silica	0·0034	0·0261	0·0024	0·0075	0·0212	0·0250
Organic matter . .	trace	trace	trace	0·0180	trace	0·0248
Total	15·5159	13·6639	4·1718	6·2231	3·9757	2·2465
Total residue (by experiment) . .	15·4780	13·5581	4·1029	6·2589	3 8935	2·2638

GRAINS OF SALINE CONSTITUENTS IN THE GALLON OF WATER.

	I. Old Sulphur Well.	II. Montpellier Strong Sulphur Well.	III. Montpellier Mild Sulphur Well.	IV. Hospital Strong Sulphur Spring.	V. Hospital Mild Sulphur Spring.	VI. Starbeck Sulphur Spa.
Sulphate of lime .	0·182	0·594	12·104	51·660	1·215	0·870
Carbonate of lime .	12·365	24·182	20·457	25·560	19·794	6·960
Fluoride of calcium	trace	trace	trace	trace		faint trace
Chloride of calcium	81·735	61·910	—	—	—	—
Chloride of magnesium	55·693	54·667	17·140	11·595	0·336	—
Carbonate of magnesia	—	—	3·251	5·797	10·310	5·390
Chloride of potassium	64·701	5·750	3·975	10·751	24·970	
Carbonate of potassa						12·207
Chloride of sodium	866·180	803·093	232·413	369·014	220·630	121·798
Bromide of sodium	trace		trace	trace	trace	trace
Iodide of sodium .	trace		trace	trace	trace	trace
Sulphide of sodium	15·479	14·414	3·398	7·155	0·301	1·711
Carbonate of soda .	—	—	—	—	—	5·133
Ammonia. . . .	trace	trace	trace	trace	trace	trace
Carbonate of iron .	trace	trace	trace	1·060	trace	trace
Carbonate of manganese.	trace	trace	trace	trace	trace	trace
Silica	0·246	1·840	0·165	0·535	1·49	1·753
Organic matter . .	trace	trace	trace	1·327	trace	1·740
Total	1096·580	966·456	292·903	437·966	279·046	157 562

GASES

DISSOLVED BY THE WATERS AND EXPELLED BY EBULLITION IN VACUO.

Composition in 100 volumes.

	I. Old Sulphur Well.	II. Montpellier Strong Sulphur Well.	III. Montpellier Mild Sulphur Well.	IV. Hospital Strong Sulphur Spring.	V. Hospital Mild Sulphur Spring.	VI. Starbeck Sulphur Spa.
Carbonic acid . .	61·06	70·62	62·50	31·79	44·07	49·78
Carbonetted hydrogen	16·17	2·71	3·99	0·52	22·80	27·71
Sulphuretted hydrogen	14·69	—	—	1·81	—	trace
Oxygen	—	2·46	—	—	7·82	—
Nitrogen	8·08	24·21	33·51	65·88	25·31	22·51
Total	100·00	100·00	100·00	100·00	100·00	100·00

CUBIC INCHES OF THE GASES IN THE GALLON OF WATER.

	I. Old Sulphur Well.	II. Montpellier Strong Sulphur Well.	III. Montpellier Mild Sulphur Well.	IV. Hospital Strong Sulphur Spring.	V. Hospital Mild Sulphur Spring.	VI. Starbeck Sulphur Spa.
Carbonic acid . .	22·03	14·01	14·28	9·54	10·20	9·26
Carbonetted hydrogen	5·84	0·53	0·90	0·15	5·28	5·15
Sulphuretted hydrogen	5·31	—	—	0·54	—	trace
Oxygen	—	0·48	—	—	1·81	—
Nitrogen	2·91	4·82	7·67	19·78	5·87	4·21
Total	36·09	19·84	22·85	30·01	23·16	18·62

TOTAL VOLUME (IN CUBIC INCHES) OF SULPHURETTED HYDROGEN IN THE SEVERAL WATERS.

I. Old Sulphur Well	24·0 Febr. 1854.	26·9 (March 1854.)
II. Montpellier Strong Sulphur Well .	23·35 May „	25·4 (May „)
III. Montpellier Mild Sulphur Well .	5·262 Febr. „	
IV. Hospital Strong Sulphur Spring .	10·888 „ „	
V. Hospital Mild Sulphur Spring . .	0·368 „ „	3·54 (March „)
VI. Starbeck Sulphur Spa	2·103 „ „	

COMPOSITION OF THE GASES (IN 100 VOLUMES) RISING FROM THE WATERS IN BUBBLES.

	I. Old Sulphur Well.	IV. Hospital Strong Sulphur Spring.
Carbonic acid	3·28	0·09
Carbonetted hydrogen . . .	40·00	—
Sulphuretted hydrogen . . .	trace	trace
Oxygen	—	—
Nitrogen	56·72	99·91
	100·00	100·00

B. CHALYBEATE WATERS.

	I. Montpellier Saline Chalybeate Water.	II. Cheltenham Saline Chalybeate Water.	III. Tewitt's Well.	IV. St. John's Well.
Temperature of air . .	44·2° F. (6·8° C.)	46·4° F. (8° C.)	49·1° F. (9·5° C.)	46·7° F. (8·2° C.)
Temperature of water .	46·4° F. (8° C.)	40° F. (4·8° C.)	46·4° F. (8° C.)	46·4° F. (8° C.)
Specific gravity . . .	1·0094	1·003	1·000108	1·00017
Reaction	markedly alkaline	very feebly alkaline	alkaline	alkaline

DIRECT RESULTS OF ANALYSIS, CALCULATED IN 1000 GRAINS

a. BASES.	Expt.	I. Montpellier Saline Chalybeate Water.	II. Cheltenham Saline Chalybeate Water.	III. Tewitt's Well.	IV. St. John's Well.
Sesquioxide of iron	I.	0·0585	0·0925	0·0270	0·0118
	II.	0·0505	0·0893	0·0266	0·012
	Mean	0·0545	0·0909	0·0268	0·01203
Manganese . .	I.	trace	trace	trace	?
	II.	—	—	—	—
	Mean	—	—	—	?
Lime	I.	1·1348	0·4252	0·0270	0·0198
	II.	1·1397	0·4232	0·0235	0·0199
	Mean	1·1372	0·4247	0·0252	0·01985
Magnesia . . .	I.	0·4952	0·2077	0·0207	0·0212
	II.	0·4985	0·2063	0·0157	0·0202
	Mean	0·4968	0·2070	0·0182	0·0207
Alkaline chlorides	I.	9·460	2·6348	0·0389	0·0593
	II.	9·454	2·6550	—	0·0545
	Mean	9·457	2·6449	0·0389	0·0584
Potassa	I.	0·1023	0·2799	0·0221	0·0096
	II.	0·1013	0·2121	—	—
	Mean	0·1018	0·2460	0·0221	0·0096
Soda	I.	4·9270	1·1607	0·0021	0·0228
	II.	4·9248	1·2364	—	—
	Mean	4·9259	1·1985	0·0021	0·0228
Ammonia . . .	I.	trace	trace	trace	trace
	II.	—	—	—	—
	Mean	—	—	—	—

DIRECT RESULTS OF ANALYSIS, CALCULATED IN 1000 GRAINS.—(*continued.*)

β. Acids, or Elements replacing them.	Expt.	I. Montpellier Saline Chalybeate Water.	II. Cheltenham Saline Chalybeate Water.	III. Tewitt's Well.	IV. St. John's Well.
Sulphuric acid	I.	absent	trace	0·0047	0·0025
	II.	—	—	0·0070	0·0025
	Mean	—	—	0·0058	0·0025
Chlorine	I.	7·5336	2·3881	0·01136	0·0134
	II.	7·5363	2·3917	0·01148	0·0134
	Mean	7·53495	2·3899	0·01142	0·0134
Bromine	I.	trace	trace	rather doubtf. tr.	?
	II.	—	—	—	—
	Mean	—	—	—	?
Iodine	I.	trace	trace	trace	?
	II.	—	—	—	—
	Mean	—	—	—	?
Fluorine	I.	absent	trace	absent	?
	II.	—	—	—	—
	Mean	—	—	—	?
Silica	I.	0·0134	0·0242	0·0159	trace
	II.	0·0134	0·0170	0·0280	—
		0·0134	0·0206	0·0220	—
Total Solid Contents.					
Mineral residue	I.	12·7961	3·9455	0·1336	0·1320
	II.	12·6372	3·9022	0·1195	0·1227
	Mean	12·7166	3·9238	0·1265	0·1278
Organic matter	I.	trace	0·0402	0·0146	trace
	II.	—	0·0398	0·0043	—
	Mean	—	0·0400	0·0095	—
Total residue	I.	12·7961	3·9857	0·1482	0·1320
	II.	12·6372	3·9420	0·1238	0·1227
	Mean	12·7166	3·9638	0·1360	0·1278

GRAINS OF SALINE CONSTITUENTS IN 1000 GRAINS.

	I. Montpellier Saline Chalybeate Water.	II. Cheltenham Saline Chalybeate Water.	III. Tewitt's Well.	IV. St. John's Well.
Sulphate of lime	—	—	0·0090	0·0043
Carbonate of lime	—	0·1590	0·0205	0·0323
Fluoride of calcium	—	trace	—	?
Chloride of calcium	2·3530	0·7351	—	—
Chloride of magnesium	0·5038	0·4845	—	—
Carbonate of magnesia	0·5880	—	0.0381	0·0434
Chloride of potassium	0·1611	0·3903	0·0189	—
Carbonate of potassa	—		0·0151	0·0141
Chloride of sodium	9·2960	2·2617	0.0040	0·0220
Bromide of sodium	trace	trace	trace	?
Iodide of sodium	trace	trace	trace	?
Carbonate of soda	—	—	—	0·0191
Ammonia	trace	trace	trace	trace
Carbonate of iron	0·0395	0·0659	0·0194	0·0087
Carbonate of manganese	trace	trace	trace	?
Silica	0·0134	0·0206	0·0220	trace
Organic matter	trace	0·0400	0.0095	trace
Total	12·9548	4·1071	0·1565	0·1439
Total residue (by experiment)	12·7561	4·0096	0·1554	0·1365

GRAINS OF SALINE CONSTITUENTS IN THE GALLON OF WATER.

	I. Montpellier Saline Chalybeate Water.	II. Cheltenham Saline Chalybeate Water.	III. Tewitt's Well.	IV. St. John's Well.
Sulphate of lime	—	—	0·697	0·307
Carbonate of lime	—	7·604	1·435	2·264
Fluoride of calcium	—	trace	—	?
Chloride of calcium	159·278	51·629	—	—
Chloride of magnesium	35·635	34·027	—	—
Carbonate of magnesia	41·796	—	2·667	3·039
Chloride of potassium	11·383	27·410	1·323	
Carbonate of potassa	—	—	1·057	0·991
Chloride of sodium	656·838	158·840	0 280	1·543
Bromide of sodium	trace	trace	trace	?
Iodide of sodium	trace	trace	trace	?
Carbonate of soda	—	—	—	1·338
Ammonia	trace	trace	trace	trace
Carbonate of iron	2·790	4·627	1·358	0·609
Carbonate of manganese	trace	trace	trace	?
Silica	0·947	1·450	1·041	trace
Organic matter	trace	0·282	0·663	trace
Total	908·667	285·869	11·021	10·091

GASES

DISSOLVED BY THE WATERS AND EXPELLED BY EBULLITION IN VACUO.

Composition in 100 volumes.

	I. Montpellier Saline Chalybeate Water.	II. Cheltenham Saline Chalybeate Water.	III. Tewitt's Well.	IV. . John's Well.
Carbonic acid	71·83	76·4	66·66	67·63
Carbonetted hydrogen	7·15	19·6	—	0·68
Oxygen	1·52	4·0	2·82	3·04
Nitrogen	19·50		30·52	28·65
	100·00	100·00	100·00	100·00

CUBIC INCHES OF THE GASES IN THE GALLON OF WATER.

	I. Montpellier Saline Chalybeate Water.	II. Cheltenham Saline Chalybeate Water.	III. Tewitt's Well.	IV. St. John's Well.
Carbonic acid	24·17	19·50	11·85	14·95
Carbonetted hydrogen	2·40	5·00	—	0·15
Oxygen	0·51	1·02	0·40	0·67
Nitrogen	6·48		5·53	6·35
	33·56	25·52	17·98	22·12

I cannot conclude this Report without expressing my thanks to Dr. Bennett, of Harrogate. His active co-operation in collecting the waters and gases, and in the analytical determinations which had to be performed at the wells, have materially facilitated and furthered this inquiry. My best thanks are also due to Messrs. A. B. Northcote and H. M. Witt, Assistants in the Royal College of Chemistry, whose zeal and talent have never failed me during the prosecution of this long investigation.

A. W. HOFMANN.

ROYAL COLLEGE OF CHEMISTRY:
JUNE 27, 1854.

Note on the Decomposition of Sulphuric Acid by Pentachloride of Phosphorus.*

By Alexander Williamson, Ph.D., F.C.S.

Chemists have long been aware of the fact that some acids unite with bases in one proportion only, others in two or more proportions. Thus a given quantity of nitric acid forms, with what is termed its equivalent of potash, a definite nitrate of potash; if less than this equivalent quantity of potash were added to the nitric acid, the product would be a mechanical mixture of the same nitrate of potash with uncombined nitric acid; if more than the equivalent of potash were added, the excess of alkali would remain uncombined. Sulphuric acid, on the other hand, is capable of forming two compounds with potash, and it depends upon the proportions in which the two substances are brought together, whether the neutral or acid sulphate is formed.

The number of compounds which an acid forms with one base is now considered as indicating its atomic weight. The weights of sulphuric and nitric acids which are respectively susceptible of neutralising the same quantity of potash, are termed *equivalent*, but these are by no means the same as their *atomic* weights. Sixty-three parts of nitric acid (nitrate of water) contain the same quantity of hydrogen as forty-five parts of sulphuric acid, and when they are neutralised by potash the whole of this hydrogen is removed, and replaced by potassium; and if neither of the acids could combine in any other proportion with potash, their atomic weights would be the same as their equivalent weights. But sulphuric acid also forms a potash-compound in which half of its hydrogen is replaced by potassium, the other half remaining in the compound, whereas the smallest particles of nitric acid either exchange the whole or none of their hydrogen for potassium.

This fact is expressed in the simplest possible manner by the statement that the smallest indivisible particles of sulphuric acid contain two atoms of hydrogen, whilst those of nitric acid only contain one. Thus it is, that whereas the equivalent weights of the two acids are the quantities which contain the same amount of basic hydrogen, their atomic weights must be in the proportion of two equivalents of sulphuric to one of nitric acid. The simplest expression for an atom of nitric acid being empirically NO_3H, we shall accordingly represent an atom of sulphuric acid by the formula SO_4H_2. In like manner, an atom of common phosphoric acid, being tribasic, is expressed empirically by the formula PO_4H_3. The labours

* Proceedings of the Royal Society, vii. 11.

of Messrs. Laurent and Gerhardt greatly contributed to the establishment of these results, which are uncontroverted.

We have hitherto been accustomed to resort very freely to imaginary distinctions of form and arrangement of matter to explain the differences of properties; but of late years an opposite tendency has arisen, and chemists have felt the necessity of reducing their language and ideas to simpler and more consistent forms. This necessity was first felt in the most complex, *i. e.* the so-called organic, part of chemistry. But the simplifications thus introduced have proved to be equally applicable to the inorganic part of the science; and their introduction is calculated to disengage, for the consideration of substantial differences of composition, the attention which has hitherto been absorbed by imaginary distinctions of form. Being unable to express the constitution of compounds without some formal artifice, we shall be able to see and compare their substantial differences most easily when all unnecessary variations of those formal artifices are eliminated. The success of this operation of course depends on our finding one form sufficiently general to replace the special and limited forms now employed.

In some papers published in the Journal of the Chemical Society two or three years ago, I endeavoured to show that the constitution of salts may be reduced to the type of water; that acids and bases, being truly acid salts and basic salts, are perfectly conformable to the same principle; and that, amongst other things, the difference between monobasic and bibasic acids, &c. admits of a simple and easy explanation by it. The leading propositions in those papers have been adopted by several eminent chemists in this country and in France; and M. Gerhardt speedily enriched science with a series of brilliant and striking illustrations of their truth. As regards the constitution of bibasic acids, M. Gerhardt's results were, however, at variance with that theory; and he was led to represent them by formulæ equally inconsistent with his own previous views on the subject. I believe that this discrepancy is satisfactorily removed by the facts I have the honour of submitting to the consideration of the Society.

An atom of nitric acid, being eminently monobasic, is, as we have already shown, represented in the monobasic type $\begin{matrix}H\\H\end{matrix}O$ by the formula $\begin{matrix}(NO_2)\\H\end{matrix}O$, in which peroxide of nitrogen (NO_2) replaces one atom of hydrogen. In like manner, hydrate of potash $\left(\begin{matrix}H\\K\end{matrix}O\right)$ is obtained by replacing one atom of hydrogen in the type by its equivalent of potassium; and nitrate of potash $\left(\begin{matrix}NO_2\\K\end{matrix}O\right)$ by a simultaneous substitution of *one* atom of hydrogen by peroxide of nitrogen, the *other* by potassium. Sulphuric acid is formed from two atoms of

water $\begin{matrix} H \\ H \end{matrix}\!O$, $\begin{matrix} H \\ H \end{matrix}\!O$; one of hydrogen from each is removed, and the two replaced by the indivisible radical SO_2. The series

Sulphuric acid.	Acid sulphate of potash.	Neutral sulphate of potash.
$\begin{matrix} H \\ SO_2 \\ H \end{matrix}\!O$,	$\begin{matrix} H \\ SO_2 \\ K \end{matrix}\!O$,	$\begin{matrix} K \\ SO_2 \\ K \end{matrix}\!O$

explains itself.

Chemists have long known how to remove the basylous constituents H, K, &c. of these salts, and to replace them by others. But it is only recently that they have learnt to remove the chlorous radicals SO_2, NO_2, &c. in a similar manner. To obtain the chloride of potassium from its sulphate, it is sufficient to bring the latter into liquid contact with chloride of barium; but the same reagent would be powerless for the preparation of the chlorides of the radicals SO_2 or NO_2.

M. Cahours has shown us a reagent (the pentachloride of phosphorus) which is capable of forming from a great number of monobasic acids the chlorides of the acid radicals. Whilst extending our knowledge of the action of the body on monobasic and organic acids, and preparing numerous compounds of their radicals with one atom of chlorine, M. Gerhardt examined also the nature of its action upon bibasic acids and their compounds; and states that it consists of two successive phases—first, the liberation of the anhydrous acid; secondly, the substitution of two atoms of chlorine for one of oxygen in that anhydrous acid. These facts, if correct, would be unfavourable to the above view of the constitution of sulphuric and other bibasic acids; and M. Gerhardt adopted accordingly the old formulæ, representing in their composition an atom of water ready-formed, SO_3H_2O.

Confining my remarks for the present to the case of sulphuric acid, whose decomposition is doubtless typical of that of other bibasic acids, I may state as the result of numerous experiments with the most varied proportions of pentachloride and acid, performed on a scale of considerable magnitude, that the first action of the pentachloride consists in removing one atom of hydrogen and one of oxygen (empirically, peroxide of hydrogen) from the acid, putting in an atom of chlorine in their place, and forming the compound $\begin{matrix} H \\ SO_2 \\ Cl \end{matrix}\!O$, which is strictly intermediate between the hydrated acid and the final product SO_2Cl_2 formed by a repetition of the same process of substitution of chlorine for peroxide of hydrogen. The existence

and formation of this body, which we may call chloro-hydrated sulphuric acid, furnishes the most direct evidence of the truth of the notion, that the bibasic character of sulphuric acid is owing to the fact of one atom of its radical SO_2 replacing or (to use the customary expression) being equivalent to two atoms of hydrogen. Had this radical been divisible like an equivalent quantity of a monobasic acid, we should have obtained a *mixture*, not a *compound* of the chloride with the hydrate,—or, at least, the products of decomposition of that mixture.

Chloro-hydrated sulphuric acid boils at 145° Cent., distilling without decomposition. The intensity of its action upon water varies according to the manner in which the two bodies are brought together. When poured rapidly into a large quantity of cold water, a portion of it sinks to the bottom, and only gradually dissolves as a mixture of hydrochloric and sulphuric acids. When a small quantity of water is added to the compound, the same decomposition takes place with explosive violence. The acid dissolves chloride of sodium on the application of a gentle heat, with evolution of hydrochloric acid, giving rise to a compound of the formula $SO_2 \begin{matrix} Na \\ Cl \end{matrix} O$. When poured upon pieces of melted nitre at the atmospheric temperature, an effervescence takes place, with evolution of a colourless vapour which possesses in a striking degree the odour of aqua regia. This vapour may be dissolved in various liquids, and when decomposed by water yields nitric and hydrochloric acids. It is doubtless chloro-nitric acid, NO_2Cl. In like manner the chlorides of other inorganic acid radicals may be obtained, as from chlorates, perchlorates, sulphites, &c.; but of these and other reactions I beg leave to defer any further account until the experiments now in hand are more advanced.

From the general resemblance of properties and identity of boiling point of the chloro-hydrate with a compound discovered by Rose, and described by that eminent chemist as possessing empirically the composition $S_2O_5Cl_2$, I was led to suspect that the two might in reality be identical,—which of course would require the addition of the elements of water to Rose's formula; and several experiments I have performed afford strong confirmation of that identity. The same compound is obtained by the action of dry hydrochloric acid on anhydrous sulphuric acid; and finally, I may mention that Mr. Railton obtained a small quantity of the same substance some weeks ago in my laboratory by the action of platinum-black at a high temperature on an imperfectly-dried mixture of chlorine and sulphurous acid.

As regards the successive transformations effected in the pentachloride, I have observed the formation of Wurtz's oxychloride (the

tribasic chloro-phosphoric acid ($PO Cl_3$)), and also of a compound boiling above 145°, probably $PO_2 Cl$. Hydrated phosphoric acid is always found unless the amount of pentachloride added is very great.

On the action of Chloride of Cyanogen on the Ammonia-bases.*

By A. Cahours and Cloez.

Hofmann has shown that the only product of the mutual action of aniline and gaseous chloride of cyanogen, is the hydrochlorate of a base containing a double atom of aniline, in which 1 atom of hydrogen is replaced by an atom of aniline: this base is called *Melaniline*.

The action is easily explained by the following equation:

$$2\,C_{12}\,H_7\,N + C_2\,N\,.\,Cl = H\,Cl\,.\,C_{24}\,H_{13}\,(C_2\,N)\,N_2.$$

On the other hand, Cloez and Cannizzaro have shown that by passing a mixture of ammonia and chloride of cyanogen carefully dried into perfectly anhydrous ether, two distinct products are obtained, viz., sal-ammoniac which settles down, and cyanic amide which remains dissolved in the ether, but may be separated by distillation in the water-bath.

The formation of these products is explained by the equation:

$$2\,N\,H_3 + C_2\,N\,Cl = H\,Cl\,.\,N\,H_3 + \underbrace{N\,H_2\,.\,C_2\,N}_{\text{Cyanic amide.}}.$$

These facts rendered it interesting to inquire whether ammonia acted in this respect differently from the conjugated ammoniacal bases, or whether aniline on the contrary formed an exception with respect to these remarkable compounds. The following experiments were undertaken with the view of solving this question.

When gaseous chloride of cyanogen, pure and very dry, is passed into the middle of a solution of aniline in anhydrous ether, contained in a vessel surrounded with pounded ice, a crystalline deposit of very pure hydrochlorate of aniline is soon formed and goes on increasing. The ethereal solution, completely freed from the crystals by filtration, and subjected to distillation over the water-bath, gives off all the ether, and leaves a viscous mass which solidifies on cooling, forming a reddish mass resembling colophony in appearance, friability, conchoidal fracture, and translucence. It is completely decomposed by heat, yielding a variety of products.

* Compt. Rend. xxxviii. 354.

It is insoluble in water, but dissolves readily in alcohol and ether. On adding water to the alcoholic or ethereal solution, a viscous substance is immediately formed, which gradually changes to a crystalline product; this substance is aniline-urea. Its analysis gave the following results:

		Calculated.	Found (mean).
14 C	84	71·18	71·02
6 H	6	5·18	5·20
2 N	28	23·74	24·15
$C_{14}\ H_6\ N_2$	118	100·00	

Under these circumstances, therefore, aniline behaves just like ammonia, thus:

$$2\ C_{12}\ H_7\ N + C_2\ N\ Cl = H\ Cl\ .\ C_{12}\ H_7\ N + \underbrace{C_{12}\ H_6\ N\ .\ C_2\ N}_{\text{Cyanic anilide.}}.$$

When a mixture of equal equivalents of hydrochlorate of aniline and cyanic anilide, dissolved in alcohol, is heated for some time over the water-bath, a crystallized product is obtained, from which ammonia no longer separates any liquid product, but a concrete substance exhibiting all the properties of melaniline. Melaniline may therefore be regarded as a conjugated compound of aniline and cyanic anilide, which is always produced if the temperature rises during the reaction.

Toluidine and naphthalidam yield results exactly similar to those observed with aniline.

Ethylaniline, treated in the same manner, yields hydrochlorate of ethylaniline, and a limpid liquid which volatilizes without decomposition, boils at 271°, and is composed of:

$$C_{18}\ H_{10}\ N_2 = C_{16}\ H_{10}\ N\ .\ C_2\ N;$$

it must therefore be regarded as *Cyanic Ethylanilide.* This compound behaves like a weak base; its hydrochlorate forms with bichloride of platinum a compound which crystallizes in large orange-red prisms of great beauty.

Methylaniline and amylaniline yield similar results.

The compounds derived from ammonia by the substitution of 2 atoms of ethyl, methyl, phenyl, &c., for 2 atoms of hydrogen, differ therefore essentially from those in which only 1 atom of hydrogen is thus replaced, inasmuch as their cyanic derivatives are volatile without decomposition.

Methylamine, ethylamine, and amylamine, treated in the same manner, yield compounds analogous to those which were obtained with ammonia and aniline; diethylamine, methylethylamine, and diamylamine, on the contrary, behaved like ethylaniline.

The compounds thus obtained are weak bases, capable of uniting with concentrated acids, and forming compounds which are decomposed by excess of water.

From the preceding facts it appears that ammonia, and the bases formed from it by the substitution of different binary groups (methyl, ethyl, amyl, &c.) for hydrogen, are acted upon by gaseous chloride of cyanogen, in a manner which may be represented by the general formula:

$$2\,C_mH_nN + C_2\,N\,Cl = Cl\,H\,.\,C_mH_nN + C_{m+2}\,H_{n-1}\,N_2.$$

Thus we have:

$$2\,C_2H_5N + C_2\,N\,Cl = Cl\,H\,.\,C_2H_5N + \underbrace{C_4\quad H_4\quad N_2}_{\text{Cyanic methylamide.}},$$

$$2\,C_4H_7N + C_2\,N\,Cl = Cl\,H\,.\,C_4H_7N + \underbrace{C_6\quad H_6\quad N_2}_{\text{Cyanic ethylamide.}}.$$

$$2\,C_{10}H_{13}N + C_2\,N\,Cl = Cl\,H\,.\,C_{10}H_{13}N + \underbrace{C_{12}\quad H_{12}\quad N_2}_{\text{Cyanic amylamide.}},$$

$$2\left[\begin{matrix}C_4H_6N\\(C_4H_5)\end{matrix}\right] + C_2\,N\,Cl = Cl\,H\,.\,\begin{matrix}C_4\ H_6\ N\\(C_4H_5)\end{matrix} + \underbrace{C_{10}\quad H_{10}\quad N_2}_{\text{Cyanic diethylamide.}}.$$

When cyanic ethylamide is carefully distilled in an oil-bath, a rapid action is observed to take place at about 180° C.; a considerable quantity of a very limpid, colourless liquid, having a peculiar cyanic odour, distils over, and there remains a viscous amber-coloured substance, which solidifies completely as it cools, and may be distilled without decomposition at a temperature above 300°.

The volatile product and the solid substance appear to be formed in about equal quantities.

The solid body is a feeble baser capable of forming a crystalline compound with hydrochloric acid. This compound forms with bichloride of platinum a double salt, which is scarcely soluble in water, very soluble in alcohol, especially in hot alcohol, and is deposited, on cooling or evaporating the liquid, in beautiful yellow scales, having a slight orange tint.

The analyses of the hydrochlorate and of the platinum-salt show that the solid product is composed of:

$$C_8\,H_8\,N_4.$$

The liquid product boils regularly and without decomposition at 190°; does not appear to be capable of forming definite compounds with acids; but is resolved, under the influence either of

acids or of alkaline bases, into carbonic acid, ammonia, and diethylamine.

The analysis of this liquid and the determination of its vapour density lead to the formula

$$C_{10}\,H_{10}\,N_2 = 4 \text{ vols. vapour.}$$

The decomposition of this substance by means of hydrate of potash may be represented by the equation:

$$C_{10}H_{10}N_2 + 2KO + 4HO = 2(CO_2 . KO) + NH_3 + \underbrace{C_4H_6\,(C_4H_5)\,N}_{\text{Diethylamine.}}.$$

The compound $C_{10}\,H_{10}\,N_2 = C_8\,H_{10}\,N.\,C_2\,N$ is cyanic diethylamide. A compound identical in its properties is in fact obtained by passing a current of gaseous chloride of cyanogen through a solution of diethylamine in anhydrous ether, till it is no longer absorbed.

Methylethylamine behaves in a similar manner to diethylamine, yielding a product which volatilizes without decomposition at 175° or 176° C.

The decomposition of cyanic ethylamide into the two products just described, is easily explained by the following equation:

$$3\,C_6\,H_6\,N_2 = C_8\,H_8\,N_4 + C_{10}\,H_{10}\,N_2.$$

Cyanic methylamide and cyanic amylamide yield similar products.

Thialdine, furfurine, and other oxygenised bases are acted upon by chloride of cyanogen in a similar manner to the ammonia-bases.

The authors likewise give, at the conclusion of their paper, a very simple process for preparing chloride of cyanogen. 100 grms. of cyanide of mercury and 4 litres of water are introduced into a bottle of the capacity of about 6 litres, and the water saturated with chlorine at 0° C. A considerable quantity of hydrate of chlorine is then formed, and the cyanide of mercury is thereby converted, in the course of twenty-four hours, into chloride of mercury and chloride of cyanogen, which remains dissolved. If the liquid, thus saturated with chloride of cyanogen, be then introduced into a flask, and heated with two or three live coals, the gas is evolved, and generally carries with it a small quantity of chlorine, from which it may be freed by passing over copper-turnings, which absorb the chlorine completely at ordinary temperatures without decomposing the chloride of cyanogen; lastly, the gas may be dried by passing it over chloride of calcium.

On a new Series of Sulphuretted Acids.*

By Dr. August Kekulé.

Adopting the idea that the series of organic compounds of which sulphuretted hydrogen is the type, corresponds in every respect with the series of which water is the type, I concluded that not only mercaptans and neutral sulphides which correspond to the alcohols and ethers, but also compounds corresponding to the acids, anhydrous acids, and ethers of acids, might be produced; I therefore endeavoured to obtain reactions which would enable me to replace oxygen in the compounds of the latter series by sulphur.

Such reactions are produced by the compounds of sulphur with phosphorus—the tersulphide (P_2S_3) and the pentasulphide (P_2S_5)—which are easily obtained by fusing together amorphous phosphorus and sulphur in an atmosphere of carbonic acid; no explosion takes place, although the combination is attended with a very violent action.

Experiment has proved that these combinations of sulphur and phosphorus act on the members of the series of water in the same manner (although less violently) as the corresponding compounds of chlorine and phosphorus;—with this difference, however, that by using the chlorine compounds, the product is resolved into *two* groups of atoms, while by using the sulphur compounds there is obtained only *one* group,—a peculiarity which, according to the bibasic nature of sulphur, must have been expected. By acting on these compounds of sulphur and phosphorus with water, one atom of sulphuretted hydrogen is obtained, while the chlorides give two atoms of hydrochloric acid,

$$6\left.\begin{matrix}H\\H\end{matrix}\right\}O + P_2S = 3\left.\begin{matrix}H\\H\end{matrix}\right\}S + 2PO_3H_3$$

$$6\left.\begin{matrix}H\\H\end{matrix}\right\}O + 2P\,Cl_3 = 6H\,Cl + 2PO_3H_3.$$

Similar reactions are observed with organic compounds belonging to the series of water, with the formation of phosphorous and phosphoric acids respectively, or of a copulated acid. By acting in this way, the following series of sulphuretted organic compounds is obtained, by the side of which are placed for comparison the products formed by the action of the chlorides of phosphorus on the same substances.

Sulphuretted Hydrogen.	Hydrochloric Acid.
$\left.\begin{matrix}H\\H\end{matrix}\right\}S.$	$2H\,Cl.$

* Proceedings of the Royal Society, vii. 37.

Mercaptan. $\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}S.$	Chloride of Ethyl + Hydrochloric Acid. $C_2H_5Cl+HCl.$
Sulphide of Ethyl. $\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}S.$	Chloride of Ethyl. $2C_2H_5Cl.$
Othyl-Hydrosulphuric Acid. $\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}S.$	Chloride of Othyl + Hydrochloric Acid. $C_2H_3O,Cl+HCl.$
Othyl-Sulphide of Othyl. $\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}S.$	Chloride of Othyl. $2C_2H_3O,Cl.$
Othyl-Sulphide of Ethyl. $\left.\begin{matrix}C_2H_3O\\C_2H_5\end{matrix}\right\}S.$	Chloride of Othyl + Chloride of Ethyl. $C_2H_3O,Cl+C_2H_5Cl.$

Mercaptan is obtained by the action of tersulphide or pentasulphide of phosphorus on alcohol with extreme facility. Sulphide of ethyl may also be prepared by acting on ether in a similar manner.

Thiacetic Acid,—Sulphuretted Acetic Acid,—has been obtained by me by acting on monohydrated acetic acid with tersulphide of phosphorus. It is a colourless liquid, boiling at about 93° C., and has a peculiar odour resembling sulphuretted hydrogen and acetic acid. It dissolves potassium in the cold, and zinc on heating, with evolution of hydrogen, and gives with lead a salt less soluble than the ordinary acetate, so that it gives a precipitate with acetate of lead. By recrystallisation from water or alcohol, the lead-salt is obtained in fine silky needles, which, though quite colourless at first, are rapidly decomposed (whether in solution or in the solid form), with formation of sulphide of lead.

By analysis, I found the lead-salt contained—

Lead 58·8 per cent. Theory requires 58·0 per cent.

The acid contained—

Sulphur 41·3 per cent. Theory requires 42·1 per cent.

Thiacetic acid is also formed in small quantity, and by secondary action, by distilling pentasulphide of phosphorus with fused acetate of soda. Pentachloride of phosphorus gives a violent reaction with thiacetic acid, yielding sulphochloride of phosphorus, chloride of othyl, and hydrochloric acid,

$$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}S+PCl_5=C_2H_3OCl+HCl+PSCl_3.$$

Thiacetate of Othyl.—Sulphide of Othyl.—Anhydrous Sulphuretted Acetic Acid.—Pentasulphide of phosphorus acts but very feebly upon anhydrous acetic acid in the cold, but on heating a violent reaction takes place. By distilling the product, the anhydrous acid

is obtained in the form of a colourless liquid, boiling at about 121° C., and having an odour greatly resembling sulphuretted acetic acid. On mixing with water it falls to the bottom, without, at first, suffering any change; on standing, however, it is slowly dissolved and decomposed into sulphuretted acetic acid and ordinary acetic acid. This change takes place much more rapidly on heating,

$$\left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}S + \left.\begin{matrix}H\\H\end{matrix}\right\}O = \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}S + \left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O.$$

It appears that anhydrous sulphuretted acetic acid is also produced by acting on the othyl-sulphide of lead with chloride of othyl; at all events, chloride of lead is formed. Chloride of benzoyl gives with the lead-salt a similar reaction, and it is probable that an intermediate sulphuretted acid is formed, having the formula,

$$\left.\begin{matrix}C_2H_3O\\C_7H_5O\end{matrix}\right\}S.$$

Thiacetate of Ethyl.—Sulphuretted Acetic Ether.—This compound may be prepared by the action of pentasulphide of phosphorus on acetic ether. It is a liquid lighter than water, and possesses an odour resembling acetic ether and sulphuretted hydrogen. It boils at about 80° C.

It will be seen that the action of tersulphide and pentasulphide of phosphorus above described produces sulphuretted organic compounds by substituting sulphur for oxygen. The compounds obtained in this way may also be formed by replacing one or two atoms of hydrogen in sulphuretted hydrogen (H_2S), or one or two atoms of metal in sulphide of potassium (K_2S), or in sulphide of hydrogen and potassium (KHS), by organic radicals. Mercaptan and the sulphides of alcohol radicals have, in fact, been long obtained in this manner.

The formation of a sulphuretted compound containing an acid radical has been observed by Gerhardt by acting on sulphide of lead with chloride of othyl. I have not made many experiments of this kind, but I have observed that chloride of benzoyl is not decomposed by sulphuretted hydrogen, while it (as well as chloride of othyl) gives a reaction with sulphide of hydrogen and potassium, yielding chloride of potassium.

I am continuing these researches, and believe the above reactions will furnish many new compounds, and will tend to complete our knowledge of some of those organic and inorganic compounds now known.

On the formation of Nitride of Benzoyl from Hippuric Acid.*

By Dr. Limpricht and Von Uslar.

When hippuric acid is heated in a tubulated retort having a thermometer adapted to it, the acid melts at about 130° C.; at 210° a small deposit of benzoic acid is formed in the neck of the retort, and at 240° the mass begins to boil. The only volatile products formed in this action are benzoic acid, having a slight red colour due to the presence of a foreign body, traces of hydrocyanic acid, and a liquid body, which was found to be nitride of benzoyl.

These mixed products were distilled with water, whereupon the nitride of benzoyl passed over with the water. To purify it completely, it was rectified by itself over burnt lime.

It is a clear, strongly refracting liquid, having an odour so much like that of bitter almond oil that it was at first mistaken for that substance. Its boiling point was 192°. From this, and from the analysis, it was found, however, to be identical with the so-called nitride of benzoyl, which Fehling† obtained by distilling benzoate of ammonium-oxide. Analysis gave the following results:

	Calculation.		Limpricht and Von Uslar.	Fehling.
14 C	84	81·58	81·11	81·86
5 H	5	4·85	4·94	5·05
N	14	13·57	12·42	13·39
$C_{14} H_5 N$	103	100·00		

As this body is obtained from hippuric acid in considerable quantity, and as its odour is very much like that of bitter almond oil, it may perhaps take the place of that substance in perfumery; if so, cows' and horses' urine may become valuable to the perfumer.

If the temperature at which hippuric acid is distilled be not allowed to rise above 250° C, there remains in the retort a black resinous body which is brittle in the cold but softens even at a gentle heat; it is scarcely soluble in water, but dissolves readily in alcohol and ether. The alcoholic solution, abandoned to spontaneous evaporation, deposits after a while a brown-red, viscid mass, which solidifies as soon as the supernatant liquid is poured off; if the evaporation be continued, crystals of benzoic acid having a yellow and red colour separate together with the resin. As no other definitely characterized body could be obtained from this residue, its further investigation was postponed.

* Ann. Ch. Pharm. lxxviii. 133.

† Ibid. xlix. 91.

On the Alcohol corresponding to Benzoic Acid.*

By S. Cannizzaro.

The oil obtained by the action of an alcoholic solution of potash on oil of bitter almonds, is composed of $C_{14}\ H_8\ O_2$; it is colourless, specifically heavier than water, refracts light strongly, and boils at 204° C. Although this substance does not agree in composition with the ordinary alcohols $C_n\ H_{n+2}\ O_2$, it nevertheless behaves with reagents like an alcohol, whose aldehyde would be pure bitter almond oil, $C_{14}\ H_6\ O_2$.

Nitric acid at a gentle heat converts this new alcohol into hydride of benzoyl, and chromic acid converts it into benzoic acid. When the vapour is passed over red-hot spongy platinum, an oil is produced, specifically lighter than water, and probably consisting of $C_{14}\ H_6$.

When hydrochloric acid gas is passed into this alcohol, heat is evolved, and a liquid formed which separates into two layers, the lower being an aqueous solution of hydrochloric acid, the upper an ethereal chlorine-compound, $C_{14}\ H_7\ Cl$, derived from the alcohol, $C_{14}\ H_8\ O_2$ This ether is a strongly refracting liquid, having a very powerful odour, heavier than water, and boiling between 180° and 185°. Caustic potash converts it into chloride of potassium and the alcohol of benzoic acid. Heated over the water-bath with an alcoholic solution of ammonia, it is converted into chloride of ammonium, and a base which is crystallizable and melts at a higher temperature than toluidine.

When a solution of the alcohol of benzoic acid in acetic acid is added to a mixture of sulphuric and acetic acid, an oil is produced which floats on the the top of the liquid; this oil is the acetic ether corresponding to the alcohol—viz., $C_{18}\ H_{10}\ O_4$. It is colourless, heavier than water, boils at 210°, and has a very pleasant aromatic odour, resembling that of certain kinds of pear. When heated with solution of potash, it is resolved into acetic acid and the alcohol of benzoic acid.

This alcohol appears to be the type of a whole class of new alcohols: the author is at present engaged with a more complete investigation of it.

On an Alcohol in the Wax of the Copernicia Cerifera,

By M. S. Maskelyne,†

DEPUTY READER IN MINERALOGY IN THE UNIVERSITY OF O FORD.

"It will be a matter of interest to you to know that I have been investigating the wax from the *Copernicia cerifera*,—the wax-bearing palm of the Brazils—and have obtained from it an alcohol analogous to those discovered by yourself. The analysis of this alcohol and of the acid derived from it by oxidation (which I have prepared) agree with the formula of Melissin; the melting-point, however, of the alcohol, 89° C., and of the acid, 91° C., indicate the higher alcohol of 62 atoms of carbon. I am engaged with further experiments which I trust will shortly decide this question."

* Ann. Ch. Pharm. lxxxviii. 129. † From a letter to Mr. Brodie.

THE

QUARTERLY JOURNAL

OF THE

CHEMICAL SOCIETY.

XV.—*On the Composition of a Specimen of Atacamite from the province of Copiapo, Chili.*

By Frederick Field.

A mineral consisting essentially of chlorine, copper, and water, was originally found in the bed of the river Lipas, in the desert of Atacama in Peru, and from this circumstance it has been called *Atacamite*. Since its discovery, however, it has been observed in many other localities; in some silver mines in Peru, as well as in the copper districts of *Huasco Bajo* and *Aconcagua* in Chili, in the lavas from Vesuvius, and the mines of Schwarzenberg in Saxony. I have recently observed it in large and beautiful masses in the province of Copiapo.

The analyses by various chemists of this mineral differ very much. Proust gives the following as the constitution of a specimen from Chili:*—

Oxide of copper	76·595
Hydrochloric acid	10·638
Water	12·767
	100·000

and of one from Peru:—

Oxide of copper	70·5
Hydrochloric acid	11·4
Water	18·1
	100·0

* Ann. Ch. Phys. [2] xxxii. 49.

Klaproth finds another specimen to contain—

Oxide of copper	73·0
Hydrochloric acid	10·1
Water	16·9
	100·0

Again, Berthier has analysed two specimens of Atacamite from Cobija in Bolivia, and gives us the following as his results:—

	I.	II.
Chlorine	14·9	15·2
Copper	13·3	13·5
Oxide of copper	50·0	54·1
Water	21·8	17·2
	100·0	100·0

Having procured some beautiful specimens from this province while visiting a mine in the vicinity of Copiapo, I imagined that a brief sketch of the composition and character of the mineral would not be uninteresting, more especially as the analyses hitherto made have been somewhat conflicting, owing probably to the difficulty of obtaining specimens of sufficient purity for analysis.

The mineral from Copiapo crystallises in right rhombic prisms, as well as hexagonal tables, although I have observed them also in beautiful stellated crystals radiating from a centre. They have a deep emerald-green colour, are perfectly transparent and very lustrous, giving a pale apple-green streak, and forming a similar coloured opaque powder when crushed. Hardness about 2·6; spec. grav. 4·25. Before the blow-pipe, the mineral is reduced on charcoal, a button of metallic copper remaining; at the same time the flame is tinged with a deep blue, with green edges. The mineral is perfectly soluble in ammonia, very slightly so in water. Hydrochloric and nitric acids, even when highly dilute, dissolve it without effervescence. It was associated immediately with brown oxide of iron and carbonate of lime, although in the same vein there were blue sulphides of copper, antimonial sulphide of copper (Fahlerz) and carbonates of copper, both blue and green. Analysis of the mineral gave me the following results:—

	I.	II.
Chlorine	14·94	15·01
Copper	56·46	56·24
Water	17·79	18·00

Now supposing (which is probably the case) that one equivalent of copper is associated with one of chlorine, the remainder being in the state of oxide, the following would be the constitution of the mineral:—

	I.	II.
Chloride of copper . . .	28·22	28·35
Oxide of copper	53·99	53·62
Water	17·79	18·00
	100·00	99·97

which would give very nearly the following formula:—

$$Cu\,Cl\,.\,3\,Cu\,O + 5\,H\,O.$$

The composition of the mineral from Cobija, analysed by Berthier, resembles somewhat those from Copiapo.

	From Cobija.	From Copiapo.
Chloride of copper . . .	28·2	28·22
Oxide of copper	50·0	53·99
Water	21·8	17·79
	100·0	100·00
Chloride of copper . . .	28·7	28·35
Oxide of copper	54·1	53·62
Water	17·2	18·00
	100·0	99·97

XVI.—*On the Corrosive Action of Sugar on Iron and other Metals.*

By J. H. Gladstone, Ph.D., F.R.S.

Owners of iron-built ships frequently object to sugar freights, alleging that the saccharine juices which exude from the casks rust the metal deeply. In sugar refineries also it has occasionally happened that portions of machinery made of iron have been wholly dissolved. Starting from these assertions of practical men, I have made the following observations.

If a piece of iron be partially immersed in a solution of pure cane-sugar, and it be set aside in a rather warm place, where air has

access to it, the metal will soon become deeply corroded about the edge of the liquid; but that portion which is permanently immersed will remain bright for a considerable space of time. The solution then contains protoxide of iron, which, absorbing oxygen from the atmosphere, presently separates as the sesquioxide, and subsides in the form of a red powder, leaving the sugar free to exert its influence again upon the metal. In this manner, the action becomes continuous, the organic principle acting as a carrier of oxygen; and we can readily understand how a small quantity of sugar may eat into a large sheet of iron.

A definite compound seems to be formed by the oxide of iron and sugar. It is very soluble in water, but insoluble in alcohol. Its solution is of a deep red-brown colour. It has the peculiar astringent flavour usually belonging to iron salts. The addition of ammonia or potash does not cause the precipitation of the metallic oxide; neither do alkaline carbonates; but a black precipitate is obtained at once on the addition of sulphide of ammonium, and a pale blue colour is produced by the ferrocyanide of potassium, and a deeper blue by the ferridcyanide. Nitric acid causes at once the formation of nitrous fumes, after which, neutralisation by an alkali produces an abundant precipitate of the sesquioxide. When boiled with sulphate of copper, the red oxide also precipitates. A stream of hydrosulphuric acid passed through the solution, throws down the whole of the iron as sulphide, and leaves a perfectly neutral solution, containing nothing that could be distinguished from the uncombined sugar.

This compound, then, evidently consists of protoxide of iron, with sugar but little, if at all, altered. The determination of the proportions in which these substances are combined is attended with difficulty, for the substance itself shows not the slightest disposition to crystallise; and the separation of it from uncombined sugar by means of alcohol was not found to be sufficiently practicable. The most likely way to obtain a pure substance appeared to be by allowing the sugar to saturate itself gradually with the metallic oxide.

Accordingly, some sugar solution, which had been left in a warm place with iron for eighteen months, and had evaporated to dryness during that time, was examined. When redissolved in water it contained no sugar, unless in combination with the metallic oxide; but it was not identical with the preceding compound. It was insipid, with a slight ferruginous after-taste. The action of different reagents upon it was much the same as upon that first produced; but it was much more stable, not being affected by the oxygen of the atmosphere. A stream of hydrosulphuric acid caused only a partial decomposition,

setting free a substance which had a decidedly acid reaction to test-paper, though an insipid taste. The acid thus partially separated was capable of dissolving fresh oxide of iron, but did not attack the metal itself, though immersed in it for some days.

A portion of the compound just described was evaporated to dryness in a water-bath, weighed, incinerated in a platinum crucible with the addition of a few drops of nitric acid to ensure the complete oxidation of the metal, and the sesquioxide of iron weighed.

Sugar compound taken . .	6·603 grm.
Sesquioxide of iron obtained .	1·263 „

which is equivalent to 1·136 grm. of protoxide of iron, or 17·20 per cent.

This is almost precisely what ought to be obtained from a compound of single equivalents of oxide of iron and sugar:—

	Calculated.	Found.
Protoxide of iron . . .	17·39	17·20
Sugar	82·61	82·80
	100·00	100·00

However, this must be taken rather as an approximative than as an exact expression of its composition. It is, indeed, not unlikely that the assumption of acid properties was accompanied by a slight oxidation of the organic principle. From the analogy of the baryta and lime compounds of sugar, in which that substance loses one equivalent of the elements of water in combining with the oxide, we should expect the formula of the compound first formed to be $C_{12} H_{10} O_{10}$, Fe O.

It is probable that these two are not the only compounds produced by the action of sugar on iron; for, although no indications were observed of any soluble compound of the sesquioxide, yet the red powder deposited from the solution contained more or less of some organic principle in intimate combination.

Since sugar attacks a mass of iron so readily, it seemed highly probable that it would dissolve the oxide easily; but such was not found to be the case. Some freshly-precipitated protoxide of iron, which had been well washed, was boiled in a solution of pure sugar, and set aside with it for a period of twenty-four hours in an air-tight vessel, but not a trace of iron was found in the solution. A second experiment was made, in which the oxide of iron was presented in a nascent condition to the organic principle; a solution of pure cane-sugar being mixed with one of sulphate of iron, and the whole being

just supersaturated with potash. The precipitated protoxide was separated by filtration; the solution, which was at first perfectly clear, soon became turbid from the formation of sesquioxide, but the amount of iron actually dissolved was extremely small. That the solution of even this trace depended upon the presence of the alkali, appears probable from a third experiment, where a large excess of potash was added to a similar mixture of sugar and sulphate of iron, and a deep red solution was obtained containing a large quantity of the metallic oxide. This solution, when freely exposed to the air, showed very little sign of absorbing oxygen. As a supplement to this experiment, some freshly precipitated and washed protoxide of iron was mixed with a quantity of potash in a solution of sugar contained in an air-tight vessel. After the mixture had stood awhile, protoxide of iron was found in solution; but it existed in but very small quantity, even after the expiration of a month.

In order more fully to determine the nature of this action of sugar on iron, a piece of that metal was immersed in a solution of pure sugar in a glass tube inverted over mercury, in such a way as to exclude the access of air and to retain any gas that might be formed. After the lapse of three months, it was found that not a particle of any permanent gas had been formed, and the solution remained very nearly as colourless as at first.* It thus appears that the sugar does not attack the iron as an acid does—by causing the replacement of hydrogen by the metal, and the consequent evolution of that element in the gaseous form. The presence, too, of free oxygen appears necessary to the action; and yet it has been seen by previous experiments that it is difficult to get sugar to combine with the oxide itself unless an alkali be present, when doubtless a different compound is formed.

Experiments were tried with various strengths of the saccharine solution, and with brown as well as white sugar; and in every case the iron was attacked. In order to test the effect of salts in conjunction with the sugar, pieces of iron were placed in five vessels containing equally strong solutions of cane-sugar, to four of which had been added respectively chloride of sodium, chloride of ammonium, nitrate of potash, and sulphate of magnesia. After awhile, protoxide of iron was found in all the five solutions, and there was about an equal deposit of the sesquioxide in the different cases. The addition of chloride of sodium to a mixture of freshly precipitated

* In a similar manner, iron vessels are employed without risk in sugar refineries, where the vessel is always kept filled with the saccharine solution.

protoxide of iron and sugar, did not cause combination to take place between them. A piece of zinc placed in contact with iron in the sugar solution, was found not to prevent the dissolving of that metal, but both were attacked.

The effect of a solution of sugar upon other metals was tried; but none was found to be affected by it to an extent at all comparable with iron.

Copper.—Considering the great influence which the presence of sugar exerts in preventing the precipitation of oxide of copper, it might be anticipated that it would exhibit an action on the metal itself analogous to that already described. But it is not so. In an experiment made in the summer time, a few weeks' exposure of pieces of copper to a sugar solution showed a trace of the metal dissolved; but in the winter time, an exposure of seven months' duration merely produced a very faint blueness of the saccharine liquid, which was scarcely blackened by the addition of sulphide of ammonium.

Lead.—Lead was attacked much more readily. Three days' exposure in warm weather, a few weeks in cold weather, or a few hours at a boiling temperature, produced a solution which was distinctly blackened by a soluble sulphide.

Zinc.—This metal was very slowly acted upon. Seventeen days' exposure in warm weather was found to give a solution containing some oxide of zinc; but about forty hours' boiling did not cause the solution of a sufficient quantity to be detected by the ordinary reagents. In the experiment where iron and zinc in contact were exposed to the sugar, a much larger proportion of the zinc appeared to be dissolved; after the oxidation of the iron by nitric acid and the removal of the oxide by ammonia, the alkaline solution gave a copious white precipitate when tested with hydrosulphuric acid.

Tin.—Tin was also very slowly attacked. The small quantity at any time found dissolved was in the condition of the binoxide. In an experiment in which the sugar solution was boiled with pieces of this metal for perhaps forty hours, no indication of it in the liquid was obtained.

Mercury and *Silver.*—These metals were not found to be acted upon by sugar in the slightest degree.

XVII.—*Preliminary Notice on the Action of Ammonia on the Oils and Fats.*

By Thomas H. Rowney, Ph.D., F.C.S.,

ASSISTANT IN THE COLLEGE LABORATORY, GLASGOW.

Few experiments having been made on the action of ammonia on the oils and fats, I have turned my attention to this subject, and in the laboratory of Professor Anderson, of Glasgow, have submitted several oils and fats to the action of ammonia.

As the experiments are likely to occupy some considerable length of time—owing, in most cases, to the slowness of the action—I have thought it advisable to send a short notice of some compounds already obtained, reserving for a future period the full details of my experiments.

At present I wish to confine my remarks to the compounds obtained, firstly, by the action of ammonia on almond and castor oils themselves, and secondly, to those obtained by the action of ammonia on the same oils after they have been solidified by the action of nitrous acid gas. By the action of ammonia on almond and castor oils, crystalline compounds are obtained; that from almond oil I have examined, and find it to have the formula $C_{36} H_{35} NO_2$, being that of oleamide.

The compound from castor oil, M. Bouis has examined, and he gives to it the formula $C_{36} H_{35} NO_4$, and names it Ricinolamide.* When nitrous acid gas is passed into almond or castor oil, these oils are converted into solid compounds called Elaidine and Palmine. In the case of elaidine, this change is said to be effected without any decomposition taking place, elaidic acid having the same formula as oleic acid. But according to the experiments of Playfair, a decomposition must take place when castor oil is acted upon by nitrous acid, as he gives the formula $C_{34} H_{33} O_6$ to palmic acid, which differs from that of ricinoleic acid by $C_2 H$.

To ascertain the correctness of these opinions, I have subjected elaidine and palmine to the action of ammonia, and have obtained beautiful crystalline compounds from them, differing in many respects from oleamide and ricinolamide, but having exactly the same formulæ as those two amides.

* This compound I have also obtained, but did not examine it, M. Bouis having already done so.

From these results it would appear that castor oil does not undergo any decomposition when acted upon by nitrous acid, but that the change must be similar to that which takes place in almond oil when it is subjected to the action of this acid. The formula of palmic acid should therefore be altered to $C_{36}\,H_{34}\,O_6$, palmamide being $C_{36}\,H_{35}\,NO_4$.

The following table shows the relations between these acids and amides :—

Oleic acid.	Ricinoleic acid.
$C_{36}\,H_{34}\,O_4$	$C_{36}\,H_{34}\,O_6$
Oleamide.	Ricinolamide.
$C_{36}\,H_{35}\,NO_2$	$C_{36}\,H_{35}\,NO_4$
Elaidic acid.	Palmic acid.
$C_{36}\,H_{34}\,O_4$	$C_{36}\,H_{34}\,O_6$
Elaidamide.	Palmamide.
$C_{36}\,H_{35}\,NO_2$	$C_{36}\,H_{35}\,NO_4$

I hope, in a future communication, to bring before the notice of the Society some other compounds which I have obtained.

XVIII.—*On the Substitution-Compounds obtained by the Action of Nitric Acid on Cotton.*

By Edward Ash Hadow,

student in the laboratory of king's college, london.

Analyses of Gun-cotton have been published by M. Pelouze, M. Peligot, Dr. Gladstone, Mr. Porrett, Mr. Ransome, and likewise by M. Schönbein; they, however, exhibit a remarkable want of agreement with each other, both in the formulæ to which they give rise, and in the percentage increase of weight which they would represent the cotton to have obtained on its transformation into gun-cotton.

M. Pelouze states that cotton constantly gains from 74 to 76 per cent., giving the formula $C_{24}\,H_{17}\,O_{17},5NO_5$, corresponding to an increase of 75 per cent. exactly. M. Peligot's formula is $C_{12}\,H_9\,O_9,3NO_5$, according to which the gain must be 94·4 per cent. Mr. Ransome obtained $C_{12}\,H_8\,O_{10},2NO_5$, which represents

an increase of 65·4. Dr. Gregory states it to be 69·5, which corresponds with that required by the formula which Dr. Gladstone ascribes to the most explosive gun-cotton, $C_{24}\left\{\begin{matrix}H_{15}\\5\,NO_4\end{matrix}\right\}O_{20}$, while the formula of Porrett and Teschemacher, $C_{12}H_8O_8, 4NO_5$, would *double* the original weight of the cotton. M. Schönbein gives merely the percentage of carbon, nitrogen, hydrogen, and oxygen, from which the lowest formula that can be calculated corresponds nearly to $C_{47}H_{31}O_{68}N_{10}$. In consequence of this disagreement between the formulæ, giving rise to so marked a difference in the percentage increase of weight deduced from them, it was evident that a careful determination of the weight actually acquired by cotton, after immersion in acids, ought alone to throw much light on the matter, by pointing out the formula upon which most reliance was to be placed, and from which the composition of the soluble variety might be determined, provided that it were indicated by a definite and constant increase of weight. While ascertaining this point, I was anxious likewise to discover what strength and what proportions of acids were capable of producing the soluble gun-cotton, as well as whether there were more than one such compound; expecting that, if such were the case, there would always be an increase of weight closely corresponding to two or more numbers from which formulæ might be calculated, or by which at least the results of analyses might be controlled.

In the preparation of these compounds, nitric acid was not used alone, since a very slight difference in strength produced a great difference in the result. HO, NO_5 gives an insoluble product, while $HO, NO_5 + HO$ destroys the texture of the cotton; and having ascertained that when sulphuric acid is used, no trace of it exists in any of the compounds, a mixture of the two was always used, the latter acid being advantageous for the purpose of increasing the bulk of the mixture, retaining the water abstracted from the cotton, and preventing the solution of the compound, which takes place to a greater or less extent in nitric acid alone. The mixtures were likewise made in atomic proportions, that their formulæ might be easily retained in the memory, and similar mixtures be prepared from acids of various strengths,—after some trials, those which contained 1 equiv. of monohydrated nitric acid with 2 equivs. of monohydrated sulphuric acid, proved to be best, and mixtures were made with the acids in this proportion, with from 1 to 5 additional equivs. of water—the fifth was found to disintegrate the cotton. The results obtained from 100 of cotton were as follows:—

HO, NO_5 / $2(HO, SO_3)$	HO = 177	Insoluble in ether + ⅛ alcohol, except the last, which is slightly attacked.
HO, NO_5 / $2(HO, SO_3)$	2 HO = 176	
HO, NO_5 / $2(HO, SO_3)$	3 HO = 171·7	
HO, NO_5 / $2(HO, SO_3)$	4 HO = 157	Very soluble.
HO, NO_5 / $2(HO, SO_3)$	5 HO = about 140	Soluble in great measure.

The interval between the third and fourth appeared in some degree to correspond to what had been expected; that between the fourth and fifth was doubtful, from the loss of the latter, and from its apparently containing an admixture of unchanged cotton; but on trying fractional additions of water, a corresponding intermediate increase of weight was likewise produced in the cotton: *e. g.*

HO, NO_5 / $2(HO, SO_3)$ } $3\frac{1}{3}HO = 166{\cdot}4$, HO, NO_5 / $2(HO, SO_3)$ } $3\frac{2}{3}HO = 160{\cdot}5$,

both compounds proving perfectly soluble. It was likewise found, on repeating these experiments, that it was difficult to obtain the same increase of weight unless the mixtures corresponded accurately in composition. The cotton in these experiments was thoroughly dried in a current of dry air at 212°, and in consequence of its hygroscopic properties, was weighed in the same tube in which the drying took place. At first the gun-cottons were likewise carefully dried at low temperatures, after thorough washing in distilled water; but the results not being found quite accurate, and a gradual loss of weight being observed at temperatures below 212°, the desiccation was effected by placing them *in vacuo* over sulphuric acid for twenty-four hours, after which they were found not to sustain the slightest diminution in weight. The acids were also used in large proportion to the quantity of cotton, that the water abstracted might have no appreciable effect in diluting the mixture; and as a precaution, the immersion was continued for several hours, although the full effect appears to be produced in a very short space of time. It was, however, found that, notwithstanding these advantageous conditions for the production of definite compounds, very variable increments of weight were acquired by the cotton, ranging from about 40 per cent. upwards.

Immersion in acids previously warmed was then tried, but as the cotton was found to lose weight in proportion to the duration of the

immersion, owing to a slow solution, even at 120° F., nothing could be learnt from the weighing of the compound; in other respects, however, the result of the experiment with hot acids proved curious and interesting, from the fact that $\left.\begin{matrix}\mathrm{HO,\,NO_5}\\ 2(\mathrm{HO,\,SO_3})\end{matrix}\right\}$ 3 HO, which at 60° gave rise to an almost insoluble compound, produced at 130° one perfectly soluble in ether + ⅛ alcohol: the other acid mixtures, containing *more than* 3 equivs. of water, produced soluble compounds both at 60° and 130°, but their solutions differed remarkably in one respect; for all soluble products formed at ordinary temperatures, when dissolved in the proportion of 6 grains to the ounce, give thick glutinous solutions, while all those which are the result of acids at the temperature of 130°, give perfectly fluid ones, which produce, on drying, membranes far exceeding the former in strength and toughness, and much better adapted to photographic or surgical purposes. By far the best mixture for producing collodion-wool is that represented by the formula $\left.\begin{matrix}\mathrm{HO,\,NO_5}\\ 2(\mathrm{HO,\,SO_3})\end{matrix}\right\}$ + 3½ HO, which is obtained by mixing 89 parts by weight of nitric acid sp. gr. = 1·424, with 104 parts by weight of sulphuric acid sp. gr. = 1·833. As—

$$\left.\begin{matrix}\text{Sulphuric acid, sp. gr.} = 1{\cdot}833 = 2(\mathrm{HO,\,SO_3} + \cdot 33\ \mathrm{HO}) = 103{\cdot}9\\ \text{Nitric acid, sp. gr.} = 1{\cdot}424 = \mathrm{HO,\,NO_5} + 2{\cdot}84\ \mathrm{HO} = 88{\cdot}5\end{matrix}\right\}$$

$$\mathrm{HO,NO_5} + 2(\mathrm{HO,SO_3}) + 3\tfrac{1}{2}\mathrm{HO} = 192{\cdot}4$$

These specific gravities are specially referred to, from their being those of the acids most frequently met with in commerce. Good collodion-wool is also produced by stronger acids, if there be *not less* water than that required by the formula $\left.\begin{matrix}\mathrm{HO,\,NO_5}\\ 2(\mathrm{HO,\,SO_3})\end{matrix}\right\}$ + 3 HO, and the temperature is raised to 130°; however, the stronger the acids, the more liable is the collodion-wool to become partially insoluble after drying. If there be less than three additional equivalents of water, the products are equally insoluble whether the acids are employed hot or cold.

Finding that the weighing of the product resulting from the action of warm acids could be of no service in proving the existence of definite compounds, I tried, at Mr. Hardwick's suggestion, the effect of reimmersing the cotton in a portion of the same cold acid mixture with which it had been previously treated, noting at the same time whether any second increase of weight were obtained. The results were highly satisfactory. For the preparation of the highest

compound, a mixture was made of 2 volumes of the strongest sulphuric and 1 vol. of colourless nitric acid, sp. gr. = 1·521.

27·5 grains of cotton, after some hours' immersion, weighed, after washing and drying *in vacuo*, 49·88 grains, corresponding to a gain of 81·34 per cent. In this case, it was hardly expected that a second immersion would cause an increase; by experiment it was found to have sustained a slight loss, as it now weighed 49·62, showing that the acids have a slight solvent power, even at ordinary temperatures. This increase of 81·34 per cent. in weight does not correspond with any of the analyses hitherto published, although the greatest care was taken to avoid error, on account of the important aid it would afford in deducing a formula for this and other compounds.

Another mixture, corresponding to $\left.\begin{matrix}HO, NO_5 \\ 2(HO, SO_3)\end{matrix}\right\} + 4\,HO$, gave, at the first immersion, an increase of 58·7 per cent.; by a second immersion it was found to have increased to 62·9 per cent., thus fully answering our expectations. A third immersion brought it to 64 per cent.

On account of the great difference observed between the products of $\left.\begin{matrix}HO, NO_5 \\ 2(HO, SO_3)\end{matrix}\right\} + 3\,HO$, and the same $+4\,HO$, an intermediate mixture was made. The first immersion gave an increase of 67·3 per cent.; a second immersion, 70 per cent.; a third, 71·4 per cent. Hence it was concluded that there were at least three compounds, of which from 100 of cotton there would be obtained quantities approximating to 164, 172, and 182; and it is probable that any acid mixture would produce such a definite compound, were it not diluted at the same time by the water it abstracts, which, when the dilution exceeds a certain point, gives rise to a second compound, the great mass of the liquid probably having but little influence, in consequence of the imperfect diffusion arising from the want of perfect fluidity, and the adhesion to the fibres of the cotton: the washing and *thorough* drying then enable the original acid mixture to raise the second compound to that which would have resulted in the first instance had no dilution taken place. It is evident, also, that the number of immersions required must vary, according as the acid mixture is much within or approaches near to that state of dilution which limits its power of producing a certain compound, a given quantity of water having much more effect in one case than in the other.

In trying the effect of various reagents on gun-cotton, I ascertained that it could be perfectly restored to the original cotton, without loss

of form, by means of hydrosulphuret of potassium, KS, HS. At Dr. Miller's suggestion, this was made use of to effect the analysis of the compounds, and to confirm the previous results. An aqueous solution was first tried, but found to occasion loss of weight on account of the long boiling required: an alcoholic solution was therefore prepared, by *thoroughly saturating* a strong alcoholic solution of potash with sulphuretted hydrogen, by transmitting the gas until it would absorb no more and ceased to give a precipitate in sulphate of magnesia. As, however, the reduction was found to proceed easily at ordinary temperatures, it proved better to effect the change by continuing the immersion for twenty-four hours, and thus avoid the risk of decomposition and loss which prolonged boiling occasioned. That the cotton so obtained was free from nitrogen-compounds was proved by strongly heating it with caustic potash, and conducting the gases evolved into a solution of litmus very faintly reddened, when the colour remained unchanged; by the close correspondence in the quantity obtained from gun-cotton with that originally used, or the restoration back to the original weight; and by its possessing all the physical characters of common cotton, which differs from all products obtained from it by the action of acids in its depolarising action on light, and in its far greater softness and compressibility when wet, and also by the action of $HO, SO_3 + HO$, which dissolves the nitro-compounds, producing a solution which is not blackened below 212°, while common and reduced cotton are completely carbonised below that temperature.

Two combustions of the reduced cotton have been made; one, in which the determination of hydrogen failed in consequence of an accident, gave, in 100 parts, 44·4 of carbon; another, made by Mr. Hardwick, gave—

	Found.	Calculated.	
Carbon . . .	44·86	44·44	=12 C.
Hydrogen . .	6·64	6·17	=10 H.
Oxygen . . .	48·50	49·39	=10 O.
	100·00	100·00	

The other products of the atoms of KS, HS are nitrite of potash (KO, NO_3), and a little ammonia. No trace of nitrate could be discovered in the solution, which was evaporated to dryness with excess of acetic acid to expel the nitrous acid. An attempt was made to turn the reaction of KS, HS upon gun-cotton to account in effecting the determination of the nitrogen by this

means; but the results were unsatisfactory, in consequence of the co-existence of ammonia and nitrous acid in the liquid. The solution could not be heated to expel the former without risk of loss in the weight of the reduced cotton, neither could the ammonia be retained by addition of an acid, without escape of NO_2, from the reaction of sulphuretted hydrogen and nitrous acid on each other.

An altogether different mode was therefore adopted, which consisted in making a solution of the compound in pure sulphuric acid, and after conversion of the oxides of nitrogen into nitric acid by means of some oxidating agent, estimating its amount by the method of M. Pelouze, depending on its property of converting proto- into perchloride of iron, and from the amount of the latter calculating the former. Before performing this, the properties of a solution of gun-cotton in sulphuric acid were examined. A portion, immersed in cold concentrated sulphuric acid, soon dissolves, without evolution of any gas, producing a clear, colourless solution; if this be poured at once into five or six times its bulk of water, so that the temperature does not rise before dilution takes place, the clear solution obtained gives no evidence whatever of nitric acid, or any oxide of nitrogen, even though raised subsequently to the boiling point; neither does it discolour solution of permanganate or chromate of potash. If, however, the original solution in concentrated acid be diluted with only once, or even twice, its bulk of water, a violent effervescence ensues, with abundant evolution of nitrous acid (NO_3) or peroxide of nitrogen (NO_4), together with carbonic acid. If, again, the solution in concentrated acid be heated before dilution, carbonic acid is evolved, while the oxides of nitrogen are retained, provided that the sulphuric acid is in sufficient excess: if it be now diluted with water, nitric oxide, NO_2, escapes with effervescence. It became necessary, therefore, to effect the complete conversion of the nitrogen oxides into nitric acid. After trial of various oxidising agents, the object was successfully attained by the use of bichromate of potash, which immediately peroxidises NO_3 and NO_4, but is without action on NO_2: hence it was necessary to use a solution of gun-cotton in pure sulphuric acid made *in the cold*, which was then added to a strong solution of bichromate contained in a retort; the mixture (which immediately acquired a dark green tint, from reduction of the chromic acid) was carefully distilled, precaution being taken to ensure the entire expulsion of the nitric acid, which was then estimated, as above stated, by Pelouze's method.

The quantity of cotton in a given sample of gun-cotton having been determined by reduction by KS, HS, and the nitrogen by the above

method, it is easy to see whether the compound contains any atoms of NO_5 not displacing an equivalent number of atoms of HO. The following results of analysis leave no doubt that it is purely a substitution compound:—

Compound A.—Produced by action of strongest acids, and most probably by *repeated* immersion in any mixture not weaker than $\left.\begin{matrix}HO, NO_5\\2\,(HO, SO_3)\end{matrix}\right\}+3\,HO$. Quite insoluble in any mixture of ether and alcohol, but soluble in acetic ether. Highly explosive.

I. 27·5 of pure cotton gave, by three hours' immersion in strongest acid, 49·88 first time; 49·6 second time.

II. 6·85 of this gun-cotton gave by reduction 3·78 of cotton.

III. 6·37 of gun-cotton by reduction gave 3·48 of cotton.

IV. 20·50 of gun-cotton gave $NO_5 = 10{\cdot}84$.

	By Synthesis.	By Analysis.		By Calculation.
	I.	II.	III.	$C_{36}H_{21}O_{30}\,9\,NO_4$.
Cotton found .	55·13	54·6	55·19	54·54
NO_4-H . .	—	—	44·07	45·46
			99·26	100·00

The composition of cotton being fully determined by the analyses of MM. Mitscherlich, Pelouze, and Payen, to be in the proportion of $C_{12}H_{10}O_{10}$, the preceding analysis would give rise to the formula $C_{36}\left.\begin{matrix}H_{21}\\9\,NO_4\end{matrix}\right\}O_{30}=891$.

100 cotton produced 181·34: by calculation, 183·3.

Compound B.—Produced most probably by any acids of composition intermediate between

$$\left.\begin{matrix}HO, NO_5\\2\,(HO, SO_3)\end{matrix}\right\}+3\,HO, \text{ and } \left.\begin{matrix}HO, NO_5\\2\,(HO, SO_3)\end{matrix}\right\}+4\,HO.$$

That which was examined was obtained by several immersions in $\left.\begin{matrix}HO, NO_5\\2\,(HO, SO_3)\end{matrix}\right\}+3\frac{1}{2}\,HO$. It is explosive, yet perfectly soluble in ether $+\frac{1}{8}$ alcohol; quite insoluble in acetic acid.

I. 27·6 grains of cotton gave, by first immersion in the above mixture, 46·2 grains; by the second immersion, 47·1; by the third, 47·31.

II. By reduction, 6·08 grs. of the compound gave 3·50 of cotton.

	From Synthesis. I.	By Analysis. II.	Calculated. $C_{36}H_{22}O_{30}, 8NO_4$.
Cotton found .	58·34	57·56	57·45
NO_4-H . .	—	(not determined)	42·55
			100·00

Formula would be $C_{36}\left.\begin{matrix}H_{22}\\8\,NO_4\end{matrix}\right\}O_{30}=846.$

100 of cotton produced 171·4: by calculation, 174.

Compound C.—Produced by $\left.\begin{matrix}HO, NO_5\\2\,(HO, SO_3)\end{matrix}\right\}+4\,HO$. Like the preceding, this compound is very soluble in ether, but differs from it in being likewise perfectly soluble in *glacial acetic acid*. In this, as in the former compounds, the cotton fibre is quite uninjured. It is highly combustible, rather than explosive, and burns with a slow jet of flame when rammed into a tube and ignited.

I. 24·1 grs. of cotton weighed, after first immersion, 38·26; after second immersion, 39·26; after third immersion, 39·53.

II. By reduction, 9·94 grs. of the compound gave 6·00 of cotton.

	By Synthesis. I.	By Analysis. II.	By Calculation. $C_{36}H_{23}O_{30}\,7\,NO_4$.
Cotton found .	60·96	60·36	60·67
NO_4-H . .	—	(not determined)	39·33
			100·00

Formula, $C_{36}\left.\begin{matrix}H_{23}\\7\,NO_4\end{matrix}\right\}O_{30}=801.$

100 cotton produced 164·0: by calculation, 164·8.

Compound D.—The existence, composition, and identity of this compound with xyloidine, are inferred from the following reasons:—

1st. There is a compound lower than C, since

$$\left.\begin{matrix}HO, NO_5\\2\,(HO, SO_3)\end{matrix}\right\}+4\,HO$$

produces, by one immersion, an increase of only 59 per cent., yet this product is perfectly soluble; if, however, C were the last, all products not attaining 64 per cent. in their amount of increase would contain unchanged cotton, and would be only partially soluble.

2nd. The product of the action of $\left.\begin{matrix}\mathrm{HO,\,NO_5}\\ 2\,(\mathrm{HO,\,SO_3})\end{matrix}\right\}+5\,\mathrm{HO}$, in which the texture of the cotton is more or less destroyed, is only partially soluble in ether,—cotton, apparently unchanged, remaining behind; it thus appears that the soluble portion is the lowest compound obtainable by the action of the mixed acids on cotton.

3rd. As the next member in the series, its composition would be $\mathrm{C_{36}}\left\{\begin{matrix}\mathrm{H_{24}}\\ 6\,\mathrm{NO_4}\end{matrix}\right\}\mathrm{O_{30}}$, which exactly corresponds with that assigned to xyloidine; and 100 of cotton should yield 155·5. The soluble portion of these products further corresponds with xyloidine in giving an *opaque* film on drying, and in its solubility in glacial acetic acid. Although the xyloidine of woody fibre and starch agree in composition, they may be distinguished by the action of KS, HS, which reduces each to its proximate constituents, when the usual reaction with iodine may be obtained in the one case, but not in the other.

The modifications produced by the action of hot acids have not yet been examined; there is in these cases greater difficulty of avoiding loss in washing, in consequence of their disintegrated state, if immersed sufficiently long to obtain definite compounds. It is evident, however, that there are at least two, produced respectively by $\left.\begin{matrix}\mathrm{HO,\,NO_5}\\ 2\,(\mathrm{HO,\,SO_3})\end{matrix}\right\}+3\,\mathrm{HO}$, and $+4\,\mathrm{HO}$, since the former becomes insoluble after drying, while the latter remains soluble. All the compounds soluble in ether give transparent films on drying, except D. The presence of this last-named compound is one of the causes of opacity on the drying of some collodions; the other causes are, water in the alcohol or ether, or the presence of acetic ether. All these compounds may be prepared with mixtures containing much larger proportions of sulphuric acid and water; but these have the disadvantage of rapidly dissolving the compounds if used warm.

While endeavouring to ascertain the state in which nitrogen exists in these compounds, I was led to examine the action of caustic potash on the highest compound, with which, as is well known, it produces a solution capable of reducing salts of silver to a mirror-like surface upon the vessel that contains them. The decomposition of gun-cotton by a solution of potash takes place slowly at ordinary temperatures, but almost instantly on raising it to 160°; each portion then immersed causes a considerable extrication of heat, by which the temperature is soon raised to the boiling point, and ammonia is evolved with effer-

vescence. In making the solution for examination, the temperature was kept at 150°, to avoid the formation of secondary products; at this point the gun-cotton quietly disappears without effervescence, producing at last a dark treacly fluid. This was diluted, neutralised with acetic acid, and precipitated by neutral acetate of lead; the liquid filtered from the precipitate gave a further abundant precipitate with the basic acetate, from which it was at first concluded that there were two distinct acids present; this, however, was afterwards found to arise from the solubility of the lead precipitate in the acetate of potash that had been formed, from which solution the basic acetate again precipitates it. The liquid filtered from both precipitates contained nitrite and nitrate of potash. The lead precipitates, after thorough washing on a linen filter, were diffused through water and decomposed by sulphuretted hydrogen, during which process effervescence occurred, with escape of NO_2, showing that, notwithstanding the washings the precipitates had undergone, they still retained a portion of nitrate. The brownish solution obtained was again precipitated by acetate of lead, washed, and decomposed as before, when a pale yellow strongly acid liquid was obtained, retaining the original reducing power upon the salts of silver unimpaired, and capable of rapidly decomposing carbonates with effervescence. Its power of forming crystalline salts was examined by slowly evaporating a solution of the compound on a slip of glass, and viewing it under the microscope. The ammonia-salt appearing to be the most promising, the liquid was neutralised with ammonia, and allowed to evaporate *in vacuo*. After some time little tufts of prismatic crystals formed; on examination, however, these were found to be devoid of reducing power, and proved to be oxalate of ammonia. That the oxalic acid had not been formed by the subsequent processes was proved by detecting it in the original solution of gun-cotton in cold aqueous potash. The liquid, freed from oxalic acid by nitrate of lime, was found to possess many of the characters of saccharic acid, such as its property of carrying down nitrites with its lead-salt, and its reducing power on salts of silver, which is manifested in both cases on adding to the respective solutions, a portion of a solution of nitrate of silver, ammonia sufficient to cause a clear solution, and subsequently caustic potash, without which in either case no mirror-like deposit will take place, even on boiling; in certain proportions the colour of the reduced silver is identical. Like the neutral saccharates, the neutral salts of this acid (which might be termed pyroxilic acid until its identity with some other is proved) likewise give precipitates with salts of lime, baryta, and cadmium. The principal differences between the two acids are, that no crystalline

acid pyroxalate of potash could be obtained, the solution drying *in vacuo* to a gummy mass, whereas the acid saccharate is very easily crystallised; and that the saccharates of the above-mentioned bases are far more soluble in the heat than in the cold, and are visibly crystalline under the microscope; while the pyroxalates of lime and baryta are but slightly soluble on warming the liquid, and that of cadmium does not redissolve at all on the mere application of heat, though, like the saccharate, it is readily soluble in an excess of the salt of cadmium. The precipitates are likewise all amorphous, with the exception of the lime-salt, which has the form of little nodules. I have not been able further to examine the properties of this acid, or obtain a compound with the certainty of its being sufficiently pure for analysis, in consequence of the want of crystalline form and the obstinacy with which a portion of colouring matter is retained.

XIX.—*On a New Method of Estimating Sulphur.*

By William J. Russell, F.C.S.

The methods at present in use for the estimation of sulphur, especially when it is contained in organic compounds, are well known to be very imperfect. The following research was therefore undertaken at the suggestion of Professor Bunsen, before commencing a more extended one on some compounds containing this element. The principle of the method consists in oxidating the sulphur by means of oxide of mercury, the mercurial vapour given off effectually preventing any explosion. From the analyses which have been made in order to test the accuracy of the method, it will be seen that it is inferior in this respect to none of the processes of organic analysis. The method is also easy of performance, and applicable to all substances containing sulphur. The analyses are made in the following manner:—

An ordinary piece of combustion-tube is closed at one end; for most inorganic substances, and such as are easily burnt, it need not be more than thirteen or fourteen inches in length. From two to three grms. of pure oxide of mercury are first introduced into the tube, and then a mixture of equal weights of carbonate of soda and oxide of mercury. If the substance to be analysed is a solid, the process of introduction and mixing is exactly similar to that followed

in an ordinary organic analysis. The method to be used when the substance is a volatile liquid will be described when speaking of the analysis of bisulphide of carbon. A cork with a small bent tube, which is made to dip into water, is inserted into the end of the combustion-tube, to enable the operator to regulate the stream of oxygen and condense the mercurial vapours. Before commencing the heating, the screen must be placed just in front of that part of the tube containing the substance to be analysed. Coals are then applied, so that some two inches of the tube immediately before the screen is strongly heated, and should be kept so during the whole analysis. At the same time, another part nearer the front of the tube is also heated, but not so strongly; there are thus alternate portions of the tube in which no decomposition of the oxide of mercury is taking place. In the case of a volatile liquid being analysed, this is of great importance, for if the whole of the front of the tube were heated at once, the oxide of mercury would be entirely decomposed long before the substance could be properly burnt; but by this means, not more of the tube need be heated at one time than is necessary to keep up a continuous and regular stream of oxygen. The screen should be removed as soon as that part of the tube immediately in front of it has attained a bright red heat; and in the case of a non-volatile substance, the heating may be carried on rapidly, so that the whole combustion does not take above ten or fifteen minutes. Simultaneously with the heating of the part of the tube containing the substance to be analysed, coals are applied at those places which were at first left unheated, and last of all, the tube being now at a bright red heat, the oxide of mercury first introduced is decomposed. The gas given off during the combustion, as it bubbles through the water, may from time to time be tested by means of a splinter of wood which has been ignited, in order to be sure that there is always a considerable excess of oxygen. When the oxide at the end of the tube has entirely disappeared, the whole is allowed to cool, and the contents of the tube afterwards emptied out into a beaker glass, and dissolved up in water. It will generally be found that a little oxide of mercury in some part of the tube has escaped decomposition; in case none should be present, it is well to add a little, or, what is still better, a few drops of chloride of mercury; for it often happens that a trace of sulphide of sodium is formed, which would be decomposed on acidulating the solution, and thus cause a loss of sulphur.

Hydrochloric acid is now added to the solution in the beaker, and the tube well washed out with it. If sulphide of mercury be present, the solution is warmed, and the clear liquid run through a filter; to

what remains in the beaker glass some more hydrochloric acid is added, and a small crystal of chlorate of potash; and the whole again slightly warmed. If the filter appears to have any trace of sulphide of mercury upon it, it should also be put into the solution. By this means, every trace of sulphide will in a very few minutes be found to be entirely oxidised. The solution is then filtered, and the sulphuric acid precipitated in the ordinary way by chloride of barium. The carbonate of soda in general use is well known to contain sulphuric acid and other oxides of sulphur; and from these it is almost impossible to render it entirely free. The following method was therefore adopted:—The carbonate of soda, after being made entirely anhydrous, and finely powdered, is mixed with an equal weight of oxide of mercury, and the two very thoroughly incorporated together so as to obtain a substance of perfectly uniform composition. Some thirty or forty grms. of the mixture are now weighed out and heated in a combustion-tube, and the amount of sulphuric acid which it gives carefully estimated. This correction for the excess of sulphur is then applied to all the analyses made with this mixture.

The following are some of the results which have been obtained by this process, and will show how universally it may be applied, and what accurate results it gives. In the first instance, pure crystallised sulphur was taken.

Quantity used, 0·121.

Sulphate of baryta obtained, 0·8827, corresponding to 0·121 sulphur.

With sulphocyanide of potassium, the following result was obtained:—

Quantity taken, 0·5608.

Sulphate of baryta obtained, 1·3414.

	Calculation.	Experiment.
Cyanogen	26·804	—
Potassium	40·206	—
Sulphur	32·989	32·80

In order now to test the method in a still severer manner, bisulphide of carbon was next taken, which, from the very volatile nature of the compound and the large amount of sulphur which it contains, is undoubtedly a difficult substance to analyse.

The combustion-tube to be used for bodies of this nature should be of considerable length.

To prevent loss by evaporation, the following plan was adopted. One end of the bulb to contain the liquid is, as usual, drawn out into a long and thin tube; the other, after being sealed up, is again heated, and

while soft pressed upon a flat surface, so as to make the end of that form. The bulb is filled and weighed in the ordinary manner, but introduced into the combustion-tube unbroken. Before commencing the heating, a thin glass rod is introduced into the combustion-tube and pushed so far up it as just to come in contact with the flattened end of the bulb. The screen is now put into its place, a little in front of the liquid, and the heating commenced. The coals must be applied at three different places; namely, near to the open end of the tube, immediately in front of the screen, and at a part between the two. As before stated, the part near to the screen is heated most strongly, for it is well to have one portion of the tube more free from mercurial vapours than the rest. As soon as the mercury has begun to volatilise from this part, the glass rod is pushed against the end of the bulb, thus breaking the fine extremity of it against the closed end of the combustion-tube. The rod is then withdrawn, and the cork with a bent tube may be fitted in. The iron screen should now also be removed, and a small paper one placed across the combustion-furnace a little beyond where the bulb is, so that the hot coal which is applied to drive the bisulphide of carbon out of the bulb may not immediately evaporate it. As soon as the heat from the coals, which should never be more than three or four inches from the broken end of the bulb, has made that part of the tube hot, the paper screen is removed. If the coals be farther off than this, a little of the bisulphide of carbon is apt to take fire inside the tube as it is volatilised, owing to there not being a sufficient quantity of mercurial vapour in that part, and thus cause a too rapid evolution of gas. The fire is gradually advanced to the end, and at the same time more and more of the front part of the tube brought to a state of redness. The following are the analyses of bisulphide of carbon made according to this method:—

FIRST EXPERIMENT.

Quantity taken, 0·157.
Sulphate of baryta obtained, 0·9645.

SECOND EXPERIMENT.

Quantity taken, 0·156.
Sulphate of baryta obtained, 0·9569.

	Calculation.	1st Expt.	2nd Expt.
Carbon	15·79	—	—
Sulphur	84·21	84·26	84·13

XX.—*On some New Compounds of Phosphorous Acid.*

By Robert Railton, F.C.S.,

student in the laboratory of university college.

According to Wurtz's view of the constitution of the phosphites, they are all bibasic. The crystallised hydrate of phosphorous acid contains three atoms of water, two of which are basic, and may be replaced by two atoms of a metallic oxide; but the third, he says, is inseparably bound up with the acid, and is essential to its existence as an acid. Phosphorous acid may, indeed, be regarded as phosphoric acid in which one atom of oxygen is replaced by hydrogen. According to this view, the formula of the crystallised hydrate will be $2HO, PHO_4$, and the general formula of a phosphite $2MO, PHO_4$.

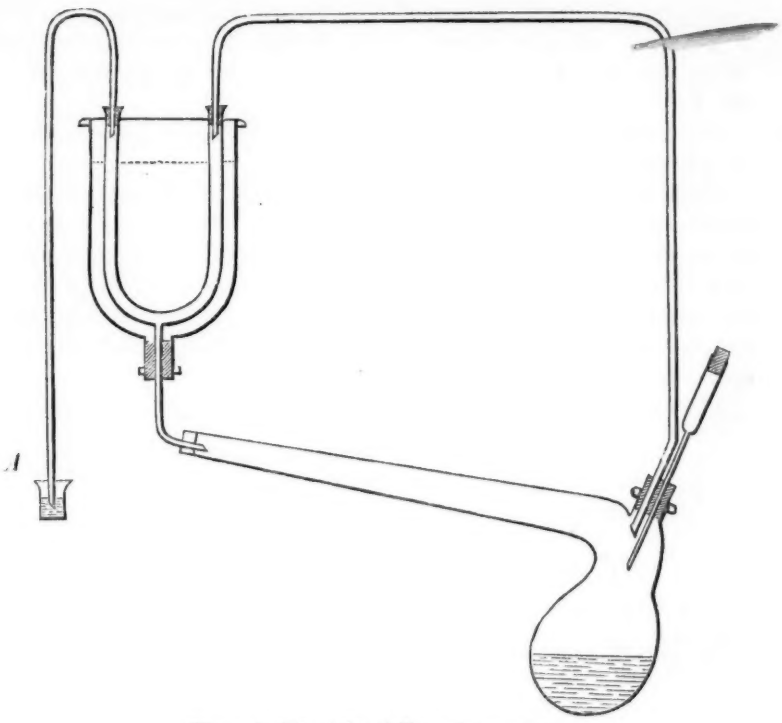
The experiments forming the subject of the present paper were made with the view of proving that the hydrogen which Wurtz considers essential to the existence of a phosphite, may be replaced by ethyl, amyl, &c.

A quantity of ethylate of soda was prepared by acting upon perfectly absolute alcohol with sodium, and evaporating to dryness at a temperature of about 120° C. A retort was used of about three times the capacity required for the bulk of ethylate of soda produced. The retort containing the dry ethylate of soda was connected with an apparatus for upward distillation, and a funnel, which admits of being closely corked, was secured in the tubulure. On the opposite page is a sketch of the apparatus used; but, of course, any other arrangement which will cause the condensed vapour to return into the retort will answer the purpose.

For every three atoms of sodium used, one atom of terchloride of phosphorus was weighed out and mixed with five times its bulk of pure ether.

This mixture was introduced into the retort by the funnel, a few drops at a time, the retort during the whole of the process being heated up to the boiling point of ether by a water-bath. The introduction of the mixture of ether and terchloride of phosphorus occupies a considerable time, and must be conducted with caution, as the action on each successive introduction is somewhat violent. After all the terchloride of phosphorus had been introduced, the heat was continued until the vapour evolved no longer reddened blue litmus paper.

The ether was then distilled off by the water-bath, the retort transferred to an oil-bath, and the oil gradually heated up to 200° C., at



The end of the tube *A* dips into mercury.

which point it was steadily maintained until the whole of the new product was eliminated.

When the operation is carefully conducted, very nearly the theoretical quantity required by the formula is obtained.

The reaction is easily explained by the following equation :—

$$3\,(NaO, C_4H_5O) + PCl_3 = 3\,C_4H_5O, PO_3 + 3\,Na\,Cl.$$

The crude product is distilled in a current of hydrogen, as it is found to oxidise if distilled in air, and that portion which comes over at 188° C. is collected and redistilled. Towards the end of each redistillation, when only a very minute quantity of the substance is left in the retort, a frothing occurs, the thermometer falls, phosphuretted hydrogen is given off, and, if the retort be opened at this juncture, the gas inflames spontaneously, with a violent explosion.

I may here mention a remarkable fact regarding the boiling point of this body. In air it is constant at 191° C.; in hydrogen at 188° C.

Phosphite of ethyl is a neutral somewhat oily substance, possessing a peculiarly offensive odour. It is soluble in water, alcohol, and ether, and burns with a bluish-white flame; its sp. gr. is 1·075 at 60° F.

The carbon and hydrogen were estimated by the ordinary method; the phosphorous acid as follows:—

Weighed quantities of the liquid were introduced into stoppered bottles, and concentrated nitric acid added. The bottles were left, loosely stoppered, in a tolerably warm situation for several days; they were then gently heated until nitrous fumes were no longer evolved. The contents of each bottle were then transferred into separate beakers, and the phosphoric acid precipitated as phosphate of magnesia and ammonia, which was ignited.

The analysis furnished the following results:—

0·2405	grm.	yielded	0·3784	grm.	of carbonic acid,
,,	,,	,,	0·1920	,,	water.
0·5115	,,	,,	0·8047	,,	carbonic acid,
,,	,,	,,	0·4155	,,	water.
0·4513	,,	,,	0·3020	,,	$2\,MgO, PO_5$.
0·4110	,,	,,	0·2780	,,	,,

The percentages are—

		Calculated.	Found.	
12 C	72	43·11	42·91	42·89
15 H	15	8·98	8·87	9·03
3 O	24	14·37	15·16	14·66
PO_3	56	33·54	33·06	33.42
	167	100·00	100·00	100·00

The vapour-density was ascertained by two experiments, conducted according to the method described by me in the Society's Journal for October 1853; and it will be seen that they agree with the calculated density:

Experimental densities	1 = 5·800
	2 = 5·877
Calculated = 4 volumes	5·763

Tribasic Phosphite of Amyl.—This body was prepared from amylate of soda, in a precisely similar manner to that described for the preparation of the ethyl-compound, and the analysis was conducted by the same process.

The production of this body may be explained by the following equation:—

$$3\,(NaO, C_{10}H_{11}O) + PCl_3 = 3\,C_{10}H_{11}O, PO_3 + 3\,NaCl.$$

Its analysis furnished the following results:—

0·2477	grm.	gave	0·5571 grm.	of carbonic acid,
„	„	„	0·2521 „	water.
0·3172	„	„	0·7123 „	carbonic acid,
„	„	„	0·3300 „	water.
1·2763	„	„	0·4855 „	2 MgO, PO_5,
1·4200	„	„	0·5405 „	„

The percentages will be as follows:—

		Calculated.	Found.	
30 C.	180	61·43	61·34	61·24
33 H	33	11·26	11·31	11·55
3 O	24	8·20	8·56	8·40
PO_3	56	19·11	18·79	18·81
	293	100·00	100·00	100·00

Phosphite of amyl is an oily neutral body, possessing a still more offensive odour than the ethyl compound, and is more easily decomposed by heat. It boils in hydrogen at 236° C., is insoluble in water, but soluble in alcohol and in ether.

Phosphite of ethyl appears to form two classes of salts, according to the amount of metallic base presented to it. Thus, by acting upon it by one and two atoms of hydrate of baryta respectively, in a manner which will be described further on, we obtain first a salt in which one atom of ethyl is replaced by one atom of barium,—a reaction which the following equation will explain:—

$$3\,C_4H_5O, PO_3 + BaO, HO = BaO, 2\,C_4H_5O, PO_3 + C_4H_6O_2.$$

The formation of the second salt may be thus explained:—

$$3\,C_4H_5O, PO_3 + 2\,(BaO, HO) = 2\,BaO, C_4H_5O, PO_3 + 2\,C_4H_6O_2.$$

I may here remark that I could not succeed in replacing the third atom of ethyl by barium.

$BaO, 2\,C_4H_5O, PO_3$.—This salt is formed when to one atom of baryta, dissolved in hot water, one atom of phosphite of ethyl is added, and the whole gently heated for a few minutes. Alcohol is given off, the liquid becomes neutral, and, if carefully evaporated in a water-bath, deposits the salt as a confused crystalline mass. This salt is extremely soluble in water, soluble in dilute alcohol, but only slightly

so in absolute alcohol. The baryta salt was recrystallised, the crystals dried between folds of blotting-paper, and then, under an exhausted receiver, over sulphuric acid, until it ceased to lose weight. It was then transferred to an oil-bath, and heated up to 108° C., which temperature does not decompose it. It is very deliquescent, and consequently the analysis shows a somewhat greater increase of hydrogen and deficiency of carbon than might be otherwise expected.

0·8320	grm.	yielded	0·6910	grm.	of carbonic acid,
„	„	„	0·3710	„	water.
1·6195	„	„	1·3505	„	carbonic acid,
„	„	„	0·7455	„	water.
1·1065	„	„	0·6285	„	BaO, SO_3,
„	„	„	0·6070	„	$2\,MgO, PO_5$.
1·1301	„	„	0·6380	„	BaO, SO_3,
„	„	„	0·6190	„	$2\,MgO, PO_5$.

From which results the following percentages were deduced:—

		Calculated.	Found.	
8 C . .	48·00	23·22	22·65	22·74
10 H . .	10·00	4·84	4·95	5·11
2 O . .	16·00	7·74	7·98	8·00
BaO .	76.64	37·09	37·32	37·09
PO_3 .	56·00	27·11	27·10	27·06
	206·64	100·00	100·00	100·00

The combustion in the first experiment was made with oxide of copper; in the second, with chromate of lead.

The baryta and phosphorous acid were estimated from the same salt. The salt was dissolved in water, and the baryta precipitated with pure sulphuric acid. The filtrate from the sulphate of baryta was then carefully evaporated to a small bulk, and the phosphorous acid oxidised by means of concentrated nitric acid, then precipitated as the phosphate of magnesia and ammonia, which was well washed, dried, and ignited.

The potash salt was obtained from the baryta salt by double decomposition with sulphate of potash. It crystallises with difficulty, in thin plates radiating from the centre; is soluble in alcohol, but not in ether, and is deliquescent.

The soda salt was obtained in a similar manner, and has similar properties. I did not succeed in crystallising it.

The nickel, zinc, iron, and magnesia salts were also formed by double decomposition with their sulphates. None of them crystallise:

they are extremely soluble in water, but appear to be insoluble in alcohol.

In attempting the formation of the copper salt, the copper was reduced, even on evaporating *in vacuo*.

2 BaO, C_4H_5O, PO_3.—When two atoms of baryta are dissolved in hot water, and one atom of phosphite of ethyl added to it, and the whole gently heated, alcohol is given off, and this salt is produced. It does not crystallise, nor do any of the salts prepared from it by double decomposition with the various sulphates.

It was dried at 108° C., and gave the following results:—

0·7025	grm. yielded	0·2495	grm. of	carbonic acid,
„	„ „	0·1305	„	water.
1·8200	„ „	1·7210	„	BaO, SO_3,
„	„ „	0·8372	„	2 MgO, PO_5.
1·1600	„ „	1·0950	„	BaO, SO_3,
„	„ „	0·5335	„	2 MgO, PO_5.

The percentages are as follows:—

		Calculated.	Found.
4 C . . .	24·00	9·75	9·69
5 H . . .	5·00	2·03	2·06
O . . .	8·00	3·25	3·40
2 BaO . .	153·28	62·23	62·13
PO_3 . .	56·00	22·74	22·72
	246·28	100·00	100·00

When more than two atoms of baryta are mixed with one atom of phosphite of ethyl, the excess of baryta is gradually deposited on evaporation as carbonate, or, if the evaporation takes place *in vacuo*, as hydrate.

This salt may be evaporated in a water-bath without decomposing, but, on boiling, it is readily decomposed into alcohol, which is given off, and diphosphite of baryta, which is deposited in shining scales.

Analysis of the deposited salt:—

1·5510	grm. yielded	1·5905	grm. of	BaO, SO_3,
„	„ „	0·7720	„	2 MgO. PO_5.
0·9605	„ „	0·9850	„	BaO, SO_3,
„	„ „	0·4780	„	2 MgO, PO_5.

From these analyses the formula of this salt will be 2 HO, 2 BaO, PO_3; or, on Wurtz's view, HO, 2 BaO, PHO_4; as will be seen by comparing the percentages.

		Calculated.	Found.	
2 HO . . .	18·00	7·92	7·99	8·04
2 BaO . .	153·28	67·44	67·42	67·38
PO_3 . .	56·00	24·64	24·59	24·58
	227·28	100·00	100·00	100·00

The analysis of this salt was conducted in a similar manner to the others, except that it was dissolved in dilute hydrochloric acid.

XXI.—*On Nitroglycerine and the Products of its Decomposition by Potash.*

By Robert Railton, F.C.S.

Sobero discovered nitroglycerine some time ago, but did not determine its composition,—probably from the fact of its being a highly explosive substance. There is, however, no danger to be apprehended from its analysis, if sufficient care be taken.

The compound from which the following results were obtained was thus prepared. Equal volumes of concentrated nitric and sulphuric acids were mixed, and cooled by immersing the flask which contained them in ice-cold water. Syrupy glycerine was then introduced into the flask, a few drops at a time, the mixture being well shaken and cooled each time. After some time, the product floated on the top as an oily substance; it was then poured into cold distilled water, and repeatedly washed in that menstruum by decantation: it was afterwards freed as much as possible from water by blotting-paper, and an attempt was made to dry it more completely under the bell-jar of the air-pump, but without success, as it was rapidly decomposed on exhausting the jar.

From this circumstance, the hydrogen could not be estimated, but the relative amounts of carbon and nitrogen were satisfactorily determined by Liebig's process.

About a gramme of the compound was mixed with as much oxide of copper as half filled a combustion-tube thirty-six inches in length. About eight inches of the remainder of the tube was filled with oxide of copper, and the tube then wholly filled with reduced copper. The tube was then enveloped in copper foil, the combustion proceeded with, and the mixed gases collected in graduated tubes over mercury.

The first portion of the gases was allowed to escape; four tubes were then filled, and the following are the results in the order in which they were collected:—

Number of tubes . . .	I.	II.	III.	IV.
Volumes of mixed gases .	101	91·5	99	97
Ditto absorbed by KO .	69	61·0	65	64
Ditto remaining gas . . .	32	30·5	34	33

There being slight discrepancies in these results, I obtained tubes more finely divided, when a second experiment gave—

Number of tubes . .	I.	II.	III.	IV.	V.
Volumes of mixed gases .	178	194	192	173	194
Ditto absorbed by potash	117	128	127	115	129
Ditto residual nitrogen .	61	66	65	58	65

Now as the composition of glycerine is well known, and as the volume of nitrogen is proved by these experiments to be half that of the CO_2 absorbed by potash, we may safely assume the following to be the change which the glycerine undergoes:—

$$C_6H_8O_6 + 3\,NO_5 = C_6 \overset{H_5}{(3\,NO_4)} O_6 + 3\,HO.$$

Nitroglycerine is heavier than water, in which it is but slightly soluble; it is soluble in alcohol and in ether. When boiled for some time with an aqueous solution of caustic potash, it is decomposed, nitrate of potash and glycerine being formed.

A solution of caustic potash in water was made of nearly the same specific gravity as the nitro-glycerine. The potash solution and the nitroglycerine were introduced into a flask and boiled for several hours; at the end, the liquid became completely homogeneous, when it was carefully neutralised with pure sulphuric acid. The sulphate of potash was crystallised out, and on further evaporation the nitrate of potash was deposited. This salt was purified by repeated re-crystallisations, and afterwards analysed.

The nitrate of potash was dried until it ceased to lose weight, and was then converted into sulphate of potash.

	Grm.
Weight of the salt used . . .	0·979
Ditto KO, SO_3 formed	0·841

Calculated percentage of KO, in KO, NO_5 = 46·54
Found in the above-named salt . . . = 46·41

I may add that the salt obtained by the decomposition of nitroglycerine exhibited all the reactions of nitrate of potash.

For the purpose of obtaining the glycerine, the solution from which the nitrate of potash had been crystallised was evaporated to a syrupy consistence, and treated with absolute alcohol. The solution of glycerine in alcohol thus obtained was evaporated in a water-bath, and the residue treated with ether, in which the nitroglycerine, had there been any undecomposed, would have been dissolved. The ether was removed without having dissolved anything, and a portion of the residue heated with bisulphate of potash, when the pungent odour of acrolein was evolved.

The decomposition of nitroglycerine by means of hydrate of potash may be represented by the equation

$$C_6\,{}^{H_5}_{3(NO_4)}O_6 + 3(KO,HO) = C_6H_8O_6 + 3(KO,NO_5).$$

Nitrobenzole was boiled with concentrated solution of caustic potash for several hours; the resulting solution evaporated nearly to dryness, water added, and again evaporated, the latter process being repeated as long as any odour was perceived. The solution was then examined for nitric acid, and distinct evidence of its presence was obtained.

XXII.—*On some New Derivatives of Chloroform.*

By George Kay,

STUDENT IN THE LABORATORY OF UNIVERSITY COLLEGE.

Every process of double decomposition may be viewed in two different ways. Thus when hydrochloric acid, Cl H, acts on hydrate of potash, $\overset{H}{K}\,\Theta$,* we may say either that the hydrogen of the one changes places with potassium of the other, or the chlorine of the one with peroxide of hydrogen, $H\Theta$, in the other. This idea is strikingly illustrated by the following experiments, in which, by the action of 1 at. chloroform, $\mathfrak{C}HCl_3$, on 3 at. ethylate of soda, $\overset{Ae}{Na}\,\Theta$, the chlorine of the former is replaced by peroxide of ethyl, $\mathfrak{C}_2H_5\Theta$, the products being 3 at. chloride of sodium, and 1 at. of a new body having the empirical formula $\mathfrak{C}_7H_{16}\Theta_3$.

$$3\,\mathfrak{C}_2\overset{H_5}{Na}\Theta + \mathfrak{C}HCl_3 = 3NaCl + \mathfrak{C}_7H_{16}\Theta_3.$$

* H=1; $\mathfrak{C}$=12; Θ=16; $\mathfrak{S}$=32.

This product may be equally well conceived to be a body in which the basic hydrogen of 3 at. alcohol is replaced by the tribasic radical of chloroform, and, according to the older theories of the capacity of saturation of salts, would contain a tribasic modification of formic acid; for it bears the same relation to formic ether that a so-called tribasic phosphate bears to a monobasic phosphate.—The following is the mode of preparation:—

Two ounces of sodium were dissolved in absolute alcohol, in a tubulated retort, and the excess of alcohol distilled off as much as possible by means of an oil-bath; pure chloroform was then added gradually to the dry mass, in the proportion of 1 equivalent to 3 equivalents of the sodium used: at first the action was very violent, and the retort required to be kept cool, to prevent loss by evaporation; the liquid was then distilled from the chloride of sodium which was formed, and subjected to a series of fractional distillations. It finally resolved itself into three portions, the first of which was small, and came over between 50° and 76° C., but chiefly between 50° and 60°; the second, which was in considerable quantity, and obtained between 78° and 79°, was nearly pure alcohol; the last portion boiled constantly at 145° to 146°, and amounted to about one-sixth of the whole liquid.

The lower portion of the distillate, obtained between 50° and 76°, had the odour of common ether; a part of it was treated with sodium, and water added, when a slight turbidity was produced, but no appearance of an oily stratum; it was tested for formic acid and chlorine, both of which were found to be present.

As the above process yielded only a small product other than alcohol, the following modification was adopted:—

As much sodium as possible was dissolved in a limited quantity of alcohol; chloroform was then added, care being taken to keep the liquid alkaline, and to ensure the decomposition of the chloroform; after which more sodium was added, and the process repeated several times until the precipitate formed became bulky. The liquid was then distilled off, and again treated with sodium and chloroform as before, and separated from the precipitate. This process was continued until 2 ounces of sodium had been used; the resulting liquid was distilled fractionally, when it divided into three portions, respectively similar in quantity, and in boiling points, to those afforded by the first experiment.

The substance which boils at 145° to 146° is a colourless, limpid liquid, slightly soluble in water, and having a peculiar aromatic odour; it

burns readily, with a blue flame and little smoke; its specific gravity is 0·8964, and at −18° C. it still remained liquid.

The following analyses were made of this body :—

I. 0·1859 grm. gave 0·3855 CO_2 and 0·1716 water
II. 0·2404 „ 0·4979 „ „ 0·2283 „

These results yield the following percentages :—

	I.	II.	Mean.
C	56·55	56·48	56·51
H	10·25	10·55	10·40
C	33·20	32·97	33·08

The following is the mean of the experiments, placed in juxtaposition with the theoretical values which correspond to the formula $C_7H_{16}O_3$:—

	Experiment.	Theory.	Difference.
C	56·51	56·75	−0·24
H	10·40	10·81	−0·41
O	33·08	32·44	+0·64

The specific gravity of the vapour of the substance was taken, and the following data and results obtained :—

Weight of globe filled with air, barometer 30·1 inches, temperature 13·6° C. . .	14·0612 grm.
Sealed the globe at 219·5° C., bar. 30·1 in.	
Weight of globe and condensed vapour, barometer 30·17 inches, temperature 10·9° C.	14·2945 „
Capacity of globe in cubic inches . . .	5·77 „
Residual air at 12·8° C., barometer 30·17 inches	0·08 cub. in.

The above data give 5·217 as the specific gravity of the vapour.

Assuming that the compound has the formula $C_7H_{16}O_3$, the theoretical specific gravity of its vapour, condensed into two volumes, would be 5·124; thus—

Experimental density . . .	5·217
Theoretical „ . . .	5·124
Difference . . .	0·093

As the methods above described yielded this body in small quantity only, it was thought that the same substance might be more readily and economically procured by making use of hydrate of potash instead of

sodium; but it was necessary in the first place to ascertain what would be the action of caustic potash on the compound.

For this purpose, a small portion was dissolved in alcohol, solid hydrate of potash added, and the liquid distilled upwards for two or three hours, and then distilled off; the residue was dissolved in water, exactly neutralised by hydrochloric acid, filtered to remove the turbidity, and then a few drops of chloride of mercury added. In a little time, and after the application of heat, a very slight precipitate was formed, having the appearance of subchloride of mercury; it was also blackened by ammonia. Sesquichloride of iron was also added to a portion of the neutral liquid, when a red colour, rather darker than that of the sesquichloride itself, appeared. As the indication of the presence of formic acid was only just perceptible, it appears that the action of potash on the compound produces that acid in very small quantity only.

Twelve ounces of solid potash and eighteen ounces of powdered quicklime were now added to rather more than three pints of absolute alcohol, and theliquid distilled upwards for five or six hours; chloroform was then added gradually, in the proportion of one equivalent to three of the potash used, the upward distillation being still continued for two or three hours; the liquid was then distilled off by the heat of an oil-bath, and submitted to a series of fractional distillations. As in the former experiments, the lowest distillate had the odour of common ether.

By this method, a small distillate was obtained which boiled constantly at 144·5° to 145° C., and was equal in bulk to about one-sixth of the chloroform used; its properties were precisely the same as those of the compound already described.

Although this method yielded only a comparatively small quantity of the substance, it was much more productive and expeditious than the one previously adopted; it was therefore repeated several times, the alcohol which was separated each time by the fractional distillations being used for dissolving the potash in the next operation.

Ultimately a considerable quantity of the compound was obtained, which enabled me to determine the boiling point more exactly: that point was now found to be constantly at 146° C.:—

The following analysis was made of this compound:—

0·2597 grm. gave 0·5410 carbonic acid, and 0·2536 water.

These numbers correspond to the following percentages, opposite to which are placed the percentages in the compound $C_7H_{16}O_3$.

Experiment.	$C_7H_{16}O_3$	Difference.
C 56·79	56·75	+0·04
H 10·82	10·81	+0·01
O 32·39	32·44	−0·05

When pentachloride of phosphorus was added to a small portion of the compound, a very dense liquid was formed, having the appearance and odour of chloroform.

One equivalent of dry hydrochloric acid was passed into 17 grms. of the compound; the gas was wholly absorbed, a considerable amount of heat being evolved, and the liquid assuming a brownish colour. The liquid, which still remained neutral after the absorption of the gas, was distilled fractionally, and finally collected in three portions. The first was about one-sixth of the whole, and came over between 20° and 50° C.; the second, about one-third, was obtained between 50° and 68°; and the last, also about a third part, passed over between 68° and 100°. The smallness of these distillates precluded any further attempts to obtain a fixed boiling point.

Two equivalents of dry hydrochloric acid were next passed into 29·6 grms. of the compound; a large proportion of the gas was absorbed, but towards the close a portion passed through the liquid. After this treatment, the liquid fumed and was highly acid; it was distilled upwards for some time, by which a portion of the free hydrochloric acid was expelled, and then distilled fractionally. Ultimately four distillates were obtained; about one-third of which came over between 56° and 60°, one-fourth between 60° and 70°; one-sixth between 70° and 80°; and one-fourth between 80° and 88°. As in the previous experiment, the numerous distillations had so much reduced the bulk of the liquid, that it became impossible to arrive at a constant boiling point.

To the lowest of the above distillates about an equal bulk of water was added: the substance floated on the surface, and seemed to be only slightly soluble in the water. It was then mixed with carbonate of soda in sufficient quantity to neutralise the free acid which yet remained, and the liquid pipetted from the water, distilled upwards for a considerable time over fused chloride of calcium, and then distilled off; it was now found to boil constantly at 55·5 C.

The distillate which had been obtained between 60° and 70°, after being treated in the same manner, also yielded a liquid which boiled at 56° C. These two products, besides agreeing in their boiling points, had each the odour of formic ether.

The following analysis was made of the product, which boiled at 55·5° C.:—

0·1815 grm. gave of CO_2, 0·2920, and of water 0.1413 grm.

These numbers furnish the following percentages:—

C = 43·85
H = 8·65

Subjoined are given the calculated percentages in formic ether, and in formic ether plus an equivalent of water:—

Formic ether.	Formic ether + an eq. of water.
C 48·64	C 43·37
H 8·10	H 8·43

The vapour-density of this body was also taken by Gay-Lussac's method; the mean of three observations gave the density as 2·439: the specific gravity of the vapour of formic ether is 2·5.

From the above results, I am led to conclude that the liquid which boiled at 55·5° was merely formic ether mixed with a small amount of water, the complete separation of which was difficult in consequence of the small quantity of the liquid operated upon.

Action of Sulphuric Acid on the compound $C_7H_{16}O_3$.

To 28·7 grms. of the compound two equivalents of mono-hydrated sulphuric acid were added. The acid sank to the bottom, and did not appear to act upon the liquid; but on a slight application of heat, the action commenced, the mixture becoming dark-coloured; after the whole of the acid had been slowly added, with constant agitation of the liquid, the mixture was cooled, and then added, a few drops at a time, to about its own bulk of water, in which was kept suspended, by continual shaking, rather more than a sufficient quantity of baryta to neutralise the acid employed; a few pieces of ice were also placed in the water; and the flask in which the operation was performed was immersed in a frigorific mixture. After the whole of the acid mixture had been added to the baryta, the liquid was found to be alkaline. It was then filtered from the precipitate, which was gelatinous, and distilled. When about five-sixths had passed over, that which remained in the retort began to froth very much, and was turbid; the distillation was therefore stopped, and the residue on cooling formed a solid crystalline mass, which was dissolved in water. The solution was very turbid, and was not rendered clear even by repeated filtration. The liquid was then transferred to a flask, about an equal bulk of absolute alcohol poured upon its surface, and then left at rest for several days.

The distillate was next saturated with carbonate of potash, when a stratum of liquid rose to the surface; this liquid was pipetted off, treated several times with carbonate of potash, and then distilled;

it boiled constantly at 80° C., and was found to be common alcohol. The lower stratum was then distilled; the crystals of carbonate of potash being removed from the retort as often as their accumulation became troublesome; when the carbonate had been wholly removed, the liquid boiled at 100° C., and was merely water.

The turbid liquid, to which alcohol had been added, was found, after standing several days, to have deposited a quantity of crystals, which were hexagonal prisms; they were insoluble in alcohol, but very soluble in water; when dried and analysed, they proved to be formiate of baryta. The liquid in which these crystals had formed was again filtered, but it still remained turbid; a portion was evaporated, and the residue dried at a low temperature until it ceased to lose weight: a quantity weighing 0·561 grm., when ignited, furnished 0·3116 grm. of sulphate of baryta, which corresponds to 55·54 per cent. Sulphovinate of baryta with two atoms of water contains 55·11 per cent. of sulphate of baryta.

The gelatinous precipitate first mentioned was now washed with a large quantity of hot water, the washings evaporated down to a small bulk, and allowed to stand for two days, when a slight crop of crystals was deposited; these crystals were insoluble in alcohol, but readily dissolved by water, and were of the same form as those previously mentioned as consisting of formiate of baryta. A considerable quantity of alcohol was now passed through the washed precipitate, reduced in bulk by evaporation on the sand-bath, and then left to evaporate at the ordinary temperature; no crystals were formed, and, when dry, a very slight quantity of an amorphous substance remained.

From these experiments it appears that the action of sulphuric acid on the compound $C_7H_{16}O_3$ gives rise to sulphovinic acid, formic acid, and alcohol; no other product was observed.

A portion of the dried substance, which was believed to be sulphovinate of baryta, was distilled with dilute sulphuric acid, when alcohol and water only passed over.

An attempt was also made to replace *two* of the equivalents of chlorine in chloroform by peroxide of ethyl. For this purpose four ounces of sodium were converted into ethylate of soda, the excess of alcohol distilled off, and the dry ethylate powdered quickly in a warm mortar. It was then added, in small portions at a time, to an excess of chloroform in a tubulated retort.* The action was very brisk,

* It was necessary to add the ethylate in powder, for when in fragments it assumed a dark brown colour, and the action of chloroform upon it was almost imperceptible.

much heat being evolved, rendering it necessary to cool the liquid after each addition of ethylate. In this manner one-half of the ethylate was added, and then the liquid was distilled off, and redistilled from a retort fitted with a thermometer; the portion obtained between 60° and 70°, being chiefly chloroform, was treated, as before, with the remaining ethylate, care being still taken to keep the chloroform in excess.

The liquid product of these operations, consisting of about half a pint, was now subjected to a series of fractional distillations, when it resolved itself into chloroform, alcohol, and a small quantity of liquid having the same boiling point and properties as the compound $C_7H_{16}O_3$, which had been already obtained.

Whilst engaged on these distillations, I observed that one portion which had come over between 60° and 82°, when repeatedly distilled, gradually lowered its highest point from 82° to 79·3°: this circumstance leads me to suspect that some other compound, having its boiling point near to that of alcohol, had in the first instance been formed, but was afterwards decomposed by the frequent distillations.

The following attempt was made to obtain a compound homologous with the $C_7H_{16}O_3$, by acting upon chloroform by amylate instead of ethylate of soda:—

Two ounces of sodium were dissolved in pure amylic alcohol, the excess of fusel oil distilled off as far as possible from the amylate of soda; chloroform then added gradually to the dry amylate, in the proportion of one equivalent to three of the sodium used; and the liquid distilled from the chloride of sodium by the heat of an oil-bath, and submitted to fractional distillation. A large proportion was found to be fusel oil; the remainder was an oily-looking liquid which boiled only at a very high temperature (between 260° and 290° C.) An attempt was made to purify this liquid, but in each distillation a considerable quantity was decomposed, even in an atmosphere of dry hydrogen, a dark-coloured resinous matter remaining in the retort. In consequence of this decomposition, and of the small quantity of the liquid available, it became impossible to obtain a constant boiling point; the repeated distillations seemed to show that a fixed point existed somewhere between 280° and 300° C.

XXIII.—*On the Constitution of Commercial Creosote from Coal-tar.*

By JAMES FAIRLIE,

STUDENT IN THE LABORATORY OF UNIVERSITY COLLEGE.

The chemical history of the compound to which Reichenbach assigns the name "Creosote" remains as yet very imperfect. Reichenbach,* Ettling,† and Gorup Besanez,‡ have successively examined the substance as found among the products of the dry distillation of wood. Ettling obtained the following results :—

	I.	II.	Mean.
C	75·72	74·53	75·12
H	7·80	7·87	7·84
O	16·48	17·60	17·04

whence he assigns to creosote the formula $C_{14}H_9O_2$, which requires 77·06 C, 8·26 H, and 14·68 O. He does not, however, give the boiling point of the liquid which he analysed. Deville§ assigns to creosote the formula $C_{14}H_8O_2$, which requires 77·77 C, 7·41 H, and 14·81 O: this agrees better with the analytical results, particularly in the hydrogen, but is yet far from satisfactory. Again, Städeler‖ remarks on Ettling's paper, that his results present a much closer agreement with the percentages for the formula $C_{12}H_7O_2$, which are 75·79 C, 7·37 H, and 16·84 O. He conceived commercial creosote to be nothing but impure hydrate of phenyl, of which the formula is undoubtedly $C_{12}H_6O_2$.

More recently this substance has been investigated by Gorup Besanez,¶ who assigns to it the formula $C_{26}H_{16}O_4$. He obtained the following results :—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
C	75·32	75·72	75·54	74·76	75·82	75·02	74·78	74·68
H	7·84	7·94	7·85	7·95	7·98	7·95	7·98	7·84
O	16·84	16·34	16·61	17·29	16·30	17·03	17·24	17·48

These give a mean of { C 75·20, H 7·91, O 16·89. } His formula requires { C 76·47, H 7·84, O 15·19 }

* Pogg. Ann. xxxi. 497; Ann. Ch. Pharm. vi. 202.

† Ann. Ch. Pharm. vi. 209.

‡ Ibid. May 1853; Pharmaceutical Journal, xiii. 289.

§ Ann. Ch. Phys. [3], xii. 228.

‖ Ann. Ch. Pharm. lxxvii. 25.

¶ Ibid. May 1853; Pharmaceutical Journal, xii. 288.

The substance analysed by Gorup Besanez was evidently impure, its boiling point ranging from 398° F. to 407° (203·3 to 208·3 C.)

The following experiments, in conjunction with those of Mr. Scrugham,* show that commercial creosote is mainly a mixture of two homologous bodies, viz. *Hydrate of Phenyl or Carbolic Acid* $= \overset{\text{H}}{\underset{\text{H}}{\text{C}_6}}\text{H}_5\text{O}$, $\text{C}_6\text{H}_6\text{O}$, and *Hydrate of Cresyl* $= \overset{\text{H}}{\underset{\text{H}}{\text{C}_7}}\text{H}_7\text{O} = \text{C}_7\text{H}_8\text{O}$.†

The temperature at which the first specimen examined distilled varied from 160° C. at the commencement to 215° towards the close of the distillation: a considerable quantity of water passed over with the first portions. During the first distillation of the crude liquid the thermometer was somewhat steady at about 184° C. (the boiling-point of hydrate of phenyl), and again, though somewhat less, at 203° C. (the boiling point assigned to creosote); about two-thirds passed over below 200° C. From this portion a considerable quantity of pure hydrate of phenyl may be obtained by fractional distillation.

The boiling point of a second specimen examined varied from 190° to 224° C.; this contained much less of hydrate of phenyl and water.

The liquid distilling between 200° and 224° was submitted to frequent fractional distillations, and ultimately an eighth of the whole quantity first taken was obtained, which distilled at 203° C. Although, on redistilling, the boiling point of this portion did not vary by so much as two degrees, yet when it was repeatedly distilled, considerable variation occurred. I had occasion to observe, during the fractional distillation of the whole quantity boiling above 200° C., that there was a uniform tendency of the boiling points to become lower on each successive distillation; nor could the distillation be effected in any case without partial decomposition, a small black residue always remaining in the retort; and the different fractions, although always colourless when first collected, invariably assumed a slight yellowish tint after keeping a few days in closely stoppered bottles. Moisture was also constantly observed in the neck of the retort on redistilling portions which had come over repeatedly at above 200° C.

Three analyses of this somewhat impure product gave per-centages for carbon not greatly differing from that required by the formula $\text{C}_7\text{H}_8\text{O}$, but the hydrogen was always in excess.

It was conceived that the substance analysed was creosote, but that

* Page 237 of this volume.

† In the remainder of this paper, the double atomic weights of carbon, oxygen, and sulphur are used; viz. $\text{C} = 12$, $\text{O} = 16$, $\text{S} = 32$.

this body must be extremely unstable, and susceptible of being by oxidation reduced to hydrate of phenyl.

A portion of the liquid, which was found to boil repeatedly at 200° C. in an atmosphere of dry hydrogen, was submitted to upward distillation for some time in an atmosphere of dry oxygen. Under these circumstances the liquid rapidly blackened, and finally became slightly viscid. Not more than two-thirds of the quantity taken could be recovered by subsequent distillation, a black tarry mass remaining in the retort. The boiling point of the quantity so obtained extended through a considerable range of temperature, a large proportion having much the same boiling point as the original liquid; another portion had a lower boiling point, and seemed to be a mixture of creosote with the hydrate of phenyl.

When the liquid obtained in the purest state by ordinary distillation is distilled in an atmosphere of dry hydrogen, by far the larger portion passes over at 200° C., a very small quantity only distilling at a somewhat lower point: this larger portion, when repeatedly redistilled in hydrogen, is found to boil constantly at that temperature (200° C.)

It must be observed, that the atmosphere in which a liquid is distilled appears considerably to affect its boiling point: in this case the change from common air to hydrogen produces a fall of not less than three degrees. The boiling-point of hydrate of phenyl does not change in any number of distillations, being constant at 184° C. in common air. Nevertheless this body boils with equal steadiness at 182° C. in an atmosphere of dry hydrogen.

The liquid boiling very constantly in hydrogen at 200° C. was burnt with oxide of copper:

I.	0·4126 grm. of the liquid gave:		1·1710	grm.	of carbonic acid,
	„	„	0·2988	„	water,
II.	0·2754	„	0·7845	„	carbonic acid,
	„	„	0·1785	„	water.

The percentages deduced from these agree much more nearly with the formula $C_{14}H_8O_2$ than with any other which has been proposed for creosote.

	Calculation.		Experiment.	
			I.	II.
C_7	=84	= 77·77	77·40	77·69
H_8	= 8	= 7·41	8·05	7·20
O	=16	= 14·82	14·55	15·11
	108	100·00	100·00	100·00

I may remark that the substance analysed agrees in its general properties with the body described by Reichenbach, viz. it is very soluble in ether, alcohol, and acetic acid, but very slightly soluble in ammonia; it is colourless, of great dispersive power, and is neutral to test-paper; with sesquichloride of iron it gives a faint violet colour. Its specific gravity, as obtained in its purest form by ordinary distillation, was 1·044 at 60° F. Reichenbach gives 1·037, and Gorup Besanez 1·0461 to 1·049.

Upon the comparatively impure substance first obtained by ordinary fractional distillation, I tried the action of various reagents, with a view more particularly to determine its constitution through the products of its decomposition. The results which I obtained are not so satisfactory as could be desired; nevertheless a brief description of them may not be without interest.

Pentachloride of phosphorus acts very strongly upon creosote, with a very abundant evolution of hydrochloric acid gas; after a while, however, it is necessary to assist the action by heat. The pentachloride was added to the creosote until no more was dissolved; the mixture was then distilled upwards, until hydrochloric acid gas was no longer evolved, and then distilled in the ordinary way; upon redistillation it began to boil at 220° C. The distillation was continued, with a thermometer in the retort, till the temperature reached 300° C., when a considerable black residue remained in the retort; a portion of this was finally forced over at a temperature apparently higher than the boiling point of mercury: these last portions of the distillate showed some disposition to crystallise. Phosphoric acid was qualitatively ascertained to be present in it in a state of combination. I believe the distillate to be a mixture of the chloride and phosphate of the radical "Cresyl," C_7H_7. I was unable to obtain either of these compounds in a state of purity, although the liquid was distilled a great number of times; but it may be observed that the greater portion of the lowest fractions were collected between 180°—190° C., between which the boiling point of the chloride probably lies.

When the supposed chloride of cresyl was mixed with ethylate of soda, and the mixture distilled upwards for some time, chloride of sodium was formed in considerable quantity; when no more appeared to be formed, the liquid was distilled off. On addition of water to this distillate, a light ethereal liquid, of an extremely fragrant odour, rose to the surface, and this, when redistilled, boiled pretty

constantly at 197° C. Its composition should be $C_9H_{12}O$: thus—

$$C_7H_7Cl + \begin{matrix}C_2H_5\\Na\end{matrix}O = \begin{matrix}C_2H_5\\C_7H_7\end{matrix}O + NaCl.$$

The results of its analysis were not satisfactory, although sufficiently near to induce the belief that it was formed: the liquid obtained was evidently not quite pure.

When equal bulks of creosote and an aqueous solution of potash of specific gravity 1·25 are mixed, and allowed to remain at rest for twenty-four hours, a crystalline compound is formed, presenting the appearance of small pearly scales, which float on the surface of the liquid; the quantity formed, however, is very inconsiderable. This salt (which has been previously noticed) is extremely unstable; when collected on a porous tile, and placed over sulphuric acid, it gradually decomposes and becomes black. It appears to be the *Cresylate of potash.*

The action of fuming nitric acid upon creosote is extremely energetic; it may, however, be controlled by adding the nitric acid in small quantities at a time, the vessel containing the creosote being surrounded by ice. During the action the colour of the liquid gradually changes to a deep red. After the addition of about an equal volume of strong nitric acid, it was observed that the liquid had separated into two layers, the upper of a deep red colour, the lower black and tarry. The upper portion, when removed and neutralised with caustic potash, solidified into a distinctly crystalline mass, sparingly soluble in cold, but readily in hot water; ·1815 grm. of this salt (which I was not able to obtain perfectly pure) gave ·0575 grm. of sulphate of potash = 17·08 per cent. of potash: the probable formula of this salt, viz. $C_7\begin{matrix}H_4(NO_2)_3\\K\end{matrix}O$, requires 16·75. There is no doubt whatever that the acid of this salt is homologue of nitro-phenisic acid, and is formed by the replacement of three atoms of hydrogen by 3 (NO_4), just as three atoms of hydrogen are similarly replaced in hydrate of phenyl.

An attempt was made to obtain an acid which should contain only one or two equivalents of NO_2. For this purpose the creosote was previously dissolved in absolute alcohol, to which nitrate of urea had been added, and acted upon by dilute nitric acid: the action in this case was moderate, but no definite result was obtained.

When equal bulks of sulphuric acid and creosote were carefully mixed, the rise of temperature was considerable, and the liquid assumed a light red colour. After allowing the mixture to stand for twenty-four

hours it was neutralised by hydrate of baryta, the excess of baryta thrown down by carbonic acid gas, and the liquid filtered and concentrated by evaporation. The aqueous solution, when evaporated to dryness, yields the salt in a white granular mass; ·7925 grm. of this salt gave ·3555 grm. sulphate of baryta = 29·47 per cent. of baryta. The formula for sulpho-cresylate of baryta, $C_7 \overset{H_7}{(Ba)} O, SO_3$, requires 29·97 per cent.

Chlorine gas is largely absorbed by creosote, the liquid assuming a bright red colour; after the action of chlorine has been continued for some time, hydrochloric acid fumes are given off. On distilling this liquid after previous washing with carbonate of soda, its boiling point was found to vary from 210° C. to 244° C. The first portions of the distillate were colourless, the last of a faint violet colour; towards the end of the distillation hydrochloric acid was given off in considerable quantity, the product being evidently decomposed.

XXIV.—*On some New Compounds of Phenyl.*

By Henry Scrugham,

student in the laboratory of university college.

Hydrated oxide of phenyl or carbolic acid was obtained in considerable quantities from commercial coal-tar creosote.

About three quarts of creosote were distilled, and all that came over between 184° C. and 202° collected; that which came over below 184° contained a large quantity of water; on a second distillation, the distillate was separated into two portions, from 184° to 196°, and from 196° to 202°, the greatest portion coming over below 197°; on a third distillation, the distillate was collected at every four degrees, and afterwards at every two degrees.

By repeated distillations the boiling point gradually lowered, about one third of the whole being collected between 184° and 188°. In distilling the portion collected from 184° to 186°, crystals were observed at the end of the tube of the retort, and in the receiver. Some of these crystals were introduced into the bottles containing the portions collected at different boiling points, and a considerable quantity was formed in those portions collected at and below 188°, but none in those portions which were collected above 188°. By this method of introducing crystals already formed into the portions col-

lected between 186 and 188°, the number of distillations required in isolating this body from creosote was considerably abridged.

In the bottles where the crystals were formed there was a considerable quantity of liquid, not crystallized; this was poured off, redistilled, and more crystals obtained from it. These were needle-shaped and had a silky lustre, and when separated from the mother liquor, distilled at 184°, and condensed in the neck of the retort into a solid mass of hydrated oxide of phenyl, having the specific gravity of 1·0627, and by analysis gave $\overset{\text{C}}{\text{C}}_6\,\text{H}_6\,\overset{\text{O}}{\text{O}}$* $= \overset{\text{C}}{\text{C}}_6\overset{\text{H}_5}{\text{H}}\overset{\text{O}}{\text{O}}$.

Chloride of Phenyl.—To prepare chloride of phenyl, said to have been obtained by Laurent and Gerhardt by the action of pentachloride of phosphorus on carbolic acid, two atoms of the pentachloride were added in small portions to five of carbolic acid. The action was at first very energetic, a considerable amount of heat was developed, and hydrochloric acid evolved; but after adding fresh portions of the pentachloride, the action ceased, and it became necessary to heat the mixture. When the whole of the pentachloride was dissolved, the mixture was distilled upwards, and when it had nearly ceased to give off hydrochloric acid, the distillate was collected. Very little came over below 200° C., but at 210° it began to distil freely, and at 240° ebullition ceased, and the temperature rose rapidly to 260°; about one-tenth of the whole came over below 240°. The mixture in the retort then began to thicken, and the colour became dark brown; at this point, the process was discontinued. The distillate thus obtained was limpid and colourless, and possessed the characteristic odour of oxychloride of phosphorus; on treating it with hot water, and afterwards with a dilute solution of potash, an oily substance collected at the bottom of the vessel, and remained unchanged after three or four washings with hot water.

On drying and distilling this substance, a small portion came over about 110°; the temperature then rose rapidly to 136°; and about two-thirds of the whole quantity came over between 140° and 146°. On submitting this to fractional distillation, the boiling point appeared to be about 138°; but the quantity was small.

To a few drops of this substance strong nitric acid was added, in order to decompose and test it for phosphorus. Very little action took place in the cold; but on heating, the nitric acid was decomposed, and nitrous fumes given off; but the substance did not blacken. On boiling this mixture with sulphuric acid, no change appeared to be produced; but on adding water, a yellow oily matter

* H=1; $\overset{\text{O}}{\text{O}}$=16; $\overset{\text{C}}{\text{C}}$=12.

was precipitated, which solidified on cooling. The liquid portion tested with chloride of ammonium, ammonia, and sulphate of magnesia, gave no evidence of the presence of phosphoric acid. To another portion of the distillate nitric acid was added, the mixture evaporated down to a small bulk, and carbonate of soda added; the whole was evaporated to dryness and ignited; the residue dissolved in water, and tested as above for phosphoric acid; but no precipitate was obtained: molybdate of ammonia likewise gave no precipitate.

The experiment of producing chloride of phenyl by the action of pentachloride of phosphorus on carbolic acid was repeated. An excess of the pentachloride was added, and the mixture distilled upwards as before, but only a very small distillate was obtained, consisting chiefly of oxychloride of phosphorus; the residue in the retort became very thick and black.

The experiment was then repeated as in the first instance, and about the same proportion of colourless liquid obtained; this was purified as before, and after subjecting it, together with the former, to a series of fractional distillations, a fixed boiling point was obtained at 136° C. This substance was tested for chlorine by burning a few drops in a glass tube with dry lime; the lime was washed out with water and a little nitric acid, the solution filtered, and nitrate of silver added, when a very decided precipitate was formed, indicating the presence of chlorine. A small portion of phenylate of soda was prepared, and a few drops of the distillate which boiled at 136° added to it; the mixture heated strongly; a little water added, the liquid filtered, and the filtrate treated with nitrate of silver, when a precipitate was formed which proved to be chloride of silver.

This liquid boiling at 136° C, is the *chloride of phenyl*; it is a colourless mobile liquid, having a fragrant odour. It is soluble in alcohol and ether; insoluble in ammonia; partially soluble in cold, but easily dissolved in hot potash.

The results obtained by the analysis of this body were not very satisfactory, owing, it is presumed, to the presence of hydrate of phenyl.

The mean of two combustions with chromate of lead gave per cent.—

C . . .	66·58
H . . .	4·93

0·3873 grms. of the substance burnt in lime gave,
0·5081 „ chloride of silver, corresponding to
30·83 per cent. of chlorine.

		Theory.	Experiment.
6 C . . .	72·0	64·00	66·58
5 H . . .	5·0	4·45	4·93
Cl . . .	35·5	31·55	30·83
$C_6 H_5 Cl$	112·5	100·00	102·34

Tribasic Phosphate of Phenyl $(C_6 H_5)_3, PO_4$.—The thick oily substance which remained in the retort after the separation of the chloride of phenyl, and appeared to be non-volatile, was treated with a strong solution of potash, which was afterwards removed by repeated washings with water; it was then dried under the receiver of the air-pump, and distilled. A small portion, having a brownish colour, came over at 200° C., and crystallised in the neck of the retort, having all the appearance of hydrate of phenyl.

The temperature gradually rose until it became necessary to remove the thermometer, after which the liquid began to distil, apparently without further decomposition; the distillate was a clear oily substance, having a yellow tinge, like that of uranium glass; towards the close of the operation, the distillate became darker, and a charred mass was left in the retort.

On a second distillation of this substance, a small portion came over slightly coloured; but the greater part was colourless when first distilled, and after standing some time acquired a yellow tinge by transmitted light; a small portion obtained towards the close of the distillation was of a light yellow colour, and a charred substance was again left in the retort. The presence of phosphoric acid in this liquid was demonstrated by mixing a few drops of the purest portion with ethylate of soda; evaporating the mixture to dryness; igniting the residue; adding the charred mass by small portions to fused nitrate of potash; dissolving the product in water; neutralising with hydrochloric acid; and testing for phosphoric acid in the ordinary way, with ammonia and a magnesia salt.

Phosphate of phenyl boils at a temperature considerably above the range of mercurial thermometers. It is inodorous, soluble in alcohol and ether, but insoluble in potash, except by boiling. It sinks in a cold solution of potash, but rises to the surface on the application of heat, and again falls to the bottom on cooling; showing that it expands by heat in a remarkable degree. It also possesses the peculiar property of epipolic diffusion; by ordinary day-light the epipolic rays, which have a fine violet tint, are visible at some distance below the surface; the flame of sulphur does not produce this effect more strongly than the light of the sun.

Some difficulty was found in burning this body, on account of the high temperature required to volatilise it.

The phosphoric acid was determined by adding a weighed portion of the substance to a strong solution of potash; the mixture was evaporated to dryness in a silver crucible, and nitrate of potash added to perfect the oxidation; this fused mass was dissolved with distilled water, boiled and filtered, the filtrate acidulated with hydrochloric acid, and again boiled to expel all the carbonic acid. Ammonia and sulphate of magnesia were then added, and the double phosphate collected on a filter, washed with ammoniacal water, dried, ignited, and weighed as pyrophosphate of magnesia.

The following were the results of analysis,—

I. 0·3026 grm. gave 0·1396 water, 0·7256 carbonic acid.
II. 0·3388 „ „ 0·1572 „ 0·8256 „

Hence in 100 parts:—

		Theory.	Experiment.			
			I.	II.	III.	Mean.
18 C	216·0	66·11	65·40	65·92	—	65·92
15 H	15·0	4·59	5·12	5·13	—	5·13
P	31·7	9·71	—	—	8·90	8·90
4 O	64·0	19·59	—	—	—	20·05
$(C_6H_5)_3, PO_4$	326·7	100·00				100·00

III. 0·8713 grm. gave
0·2794 „ pyrophosphate of magnesia, corresponding to 20·24 per cent. of phosphoric acid, or 8·90 of phosphorus.

Acetate of Phenyl, $\begin{matrix} C_2H_3O \\ C_6H_5 \end{matrix} O$.—Acetate of potash dissolved in absolute alcohol was acted upon by phosphate of phenyl. No action took place in the cold, but after distilling upwards for some time, the acetate was decomposed, and when the alcohol was distilled off the temperature rose rapidly. The distillate which came over from 180° C. to 220° was distilled fractionally, and a fixed boiling point obtained at 190°. This compound is presumed to be the acetate of phenyl; it is a colourless mobile liquid, having a peculiar aromatic odour; it is slightly soluble in water, and dissolves with decomposition in hot water.

The following results obtained by the analysis of this body show that it was not obtained in a state of purity.

I. 0·3390 grm. gave 0·2012 grm. water, 0·9003 grm. carbonic acid.
II. 0·2279 „ „ 0·1359 „ „ 0·6078 „ „

Hence in 100 parts—

		Theory.	Experiment. I.	II.	III.
8 C	. . 96	70·58	72·42	72·73	72·57
8 H	. . 8	5·88	6·59	6·62	6·60
2 O	. . 32	23·54	20·99	20·65	20·83
$C_2 H_3 \atop Ph$ O O	136	100·00	100·00	100·00	100·00

Nitrophosphate of Phenyl.—Phosphate of phenyl dissolves in fuming nitric acid with evolution of heat; on boiling the solution nitrous fumes were given off, and apparently a combination effected. A portion of the compound, when cold, boiled with hydrate of potash, yielded a yellow crystalline body on cooling. On adding cold water to the remaining portion of the compound formed by the action of nitric acid on phosphate of phenyl, a yellow oily substance was thrown down, which solidified on the application of heat; this body is probably the *nitrophosphate of phenyl*, and forms with potash a beautiful crystalline salt, which has not yet been fully examined.

Cyanide of Phenyl is obtained by the action of cyanide of potassium on the phosphate. It is decomposed by boiling, with evolution of ammonia.

Oxide of Phenyl.—A mixture of chloride of phenyl and phenylate of soda was heated with the view of obtaining the oxide of phenyl; the mixture swelled up and blackened, but no distillate was obtained. Nitric acid was added to a portion of the substance, and the solution treated with nitrate of silver; a white precipitate was obtained, showing that chloride of sodium had been formed; hence it is probable that oxide of phenyl was separated.

Hydruret of Phenyl.—Four ounces of carbolic acid were introduced into a retort, together with an equivalent of terchloride of phosphorus. The action in the cold was very moderate, but on applying heat a brisk action took place. The mixture was distilled upwards for some time, and afterwards the distillate collected: a blackened substance was left in the retort. The distillate was then distilled fractionally, a portion coming over between 80° and 90° C., the temperature gradually rising to 220°, and a black residue being again left in the retort. The first portion was redistilled, and nearly the whole came over about 80° C. This body was a colourless limpid liquid, which floated on water, and had the odour of *benzin* or *hydruret of phenyl*. On redistilling the other portions, very little came over below 186°, and it appeared to consist chiefly of hydrate of phenyl.

Iodide of Phenyl.—To a solution of 6 oz. of iodine in chloroform, hydrate of phenyl and phosphorus were added in the proportions of three equivalents of the hydrate and one of phosphorus to five of iodide, the phosphorus being introduced in very small pieces, and just sufficient heat applied to keep the mixture boiling; it was distilled upwards for about two hours, during which time a reddish crystalline substance formed in the neck of the retort. After distilling off the chloroform, there remained in the retort a thick viscid mass, apparently containing an excess of iodine: to this more hydrate of phenyl and phosphorus were added, and the mixture distilled to dryness; a considerable quantity of blackened matter remained in the retort.

The chloroform distillate, which was coloured with iodine, was redistilled, all that came over above 80° C. being kept separate, and added to the first distillate; the whole was then distilled fractionally. It began to boil at 120° C.: the last portion coming over at 220,° and the largest portion from 190° to 200°; but the whole was highly coloured by free iodine. Sulphide of ammonium was added, which quickly removed the colour, and it was observed that those portions collected above 160° C. fell to the bottom, being heavier than the sulphide of ammonium, while those portions having a lower boiling point floated on the surface.

A few drops of that which came over about 190° were added to ethylate of soda; the mixture evaporated to dryness and ignited; the charred matter added to fused nitrate of potash; and a portion of the mixture, when cold, was dissolved in distilled water, filtered, and the filtrate acidulated with nitric acid; on addition of starch-paste the characteristic blue colour gave evidence of the presence of iodine; but the small quantity thus indicated showed that the iodide of phenyl is very difficult to obtain.

To six and a half ounces of carbolic acid, fourteen ounces of iodine and three-fourths of an ounce of phosphorus were added at intervals, as the combination was effected, care being taken to keep the iodine in excess; hydriodic acid was evolved in large quantities. The process was continued for about six hours, the neck of the retort being elevated and the hydriodic acid vapour received in ammonia. When no more gas was given off, the mixture was distilled, and a large quantity of black residue was left in the retort. This experiment was repeated a second time, and the distillate submitted to fractional distillation; it appeared to separate into two bodies, the one boiling below 200°, and the other between 250° and 264° C. On adding hydrate of potash to those portions which came over below 250°, about three-fourths of the whole dissolved. The portion insoluble in

potash was washed with distilled water, dried and distilled; the greater part of it came over above 250°.

After repeated distillations of those portions which came over above 250°, a fixed boiling point was obtained at 260° C.: a few drops of this liquid were tested, and found to contain iodine.

The body thus obtained is presumed to be the *Iodide of Phenyl*; it is colourless when first obtained, but acquires a brownish colour after standing some time. I regret that I have not been able to analyse it.

XXV.— *Chemical Notes.*

By James Spencer,

STUDENT IN THE LABORATORY OF UNIVERSITY COLLEGE.

I. *On a new compound obtained from Benzol by the action of Chloride of Iodine.*

As benzol may be regarded as the hydruret of phenyl, $C_{12} H_3 . H$, it seemed probable that the action of the protochloride of iodine might lead to the formation of iodide of phenyl.

The two chlorides of iodine, I Cl and I Cl_3, appear not to be very readily obtained of definite composition.

Dry chlorine gas passed over dry iodine is readily absorbed, with production of a blood-red liquid: an excess of chlorine leads to the formation of a solid crystalline compound of a yellow colour. The first should be the protochloride, the second the terchloride, but there appears to be no definite stage in the absorption which marks the limits of the formation of the two compounds; in fact, it does not appear easy to obtain either perfectly free from the other by the direct combination of the elements.

The liquid chloride does not appear to exert any sensible action upon benzol; the solid compound which was afterwards tried exerts a very violent action.

A small quantity of benzol was added to an excess of the solid chloride of iodine (which was probably not very definite in composition, but consisted principally of the terchloride); very violent action took place, accompanied by great evolution of heat. Small quantities of benzol were added from time to time, the temperature being carefully kept down between each addition, until further addition pro-

duced no action; a considerable quantity of iodine crystallised out on cooling, and a further quantity was dissolved in the excess of benzol used.

After pouring off the excess of benzol, and removing the free iodine by means of cold alcohol, a granular solid substance remained, very slightly soluble in cold alcohol, but soluble to a considerable extent in boiling alcohol, from which it crystallises, on cooling, in small colourless needle-shaped crystals; by two or three crystallisations from boiling alcohol the substance may be obtained perfectly pure.

A small quantity of a perfectly pure specimen of this substance was fused with caustic potash; its decomposition was by no means readily effected. The potash solution, when neutralised, after decomposition, afforded a copious indication of iodine by the starch test; the existence of chlorine in the compound was also qualitatively ascertained.

The substance fuses at a temperature not greatly exceeding 100° C., and afterwards sublimes without decomposition, condensing in the cooler part of the tube in very beautiful needle-shaped crystals, some of which were nearly half an inch in length.

When more strongly heated, it is partially decomposed, violet vapours of free iodine being giving off, and a carbonaceous residue left in the tube; a portion also of the substance sublimes undecomposed.

Not having been able to make a quantitative analysis of this substance, I cannot venture to decide upon its formula.

II. *An attempt to obtain the acids homologous with Benzoic Acid from the corresponding Hydrocarbons.*

For reasons similar to the above, it seemed probable that cyanide of phenyl might be obtained from benzol by the action of chloride of cyanogen, according to the equation—

$$C_{12}H_5H + C_2NCl = C_{12}H_5C_2N + HCl.$$

The experiment was tried with every precaution, perfectly pure and dry chloride of cyanogen being passed through benzol, both dry and moist, first at the ordinary temperature, and afterwards near the boiling point of the liquid; but no reaction was obtained.

If we could obtain cyanide of phenyl in this manner, we might also, by acting upon it with alcoholic potash, obtain benzoic acid,—just as cyanide of ethyl, similarly treated, yields propionic acid; and if so, we might likewise hope by similar means to obtain from xylol the hitherto undiscovered acid homologous with benzoic acid, and having the composition $C_{18}H_{10}O_4$.

III. *On the action of Hydrochloric Acid upon a mixture of Acetone and Alcohol.*

Dr. Williamson has found that when a mixture of equivalent proportions of acetate of soda and valerate of potash is submitted to dry distillation, the principal product is neither acetone nor valerone, but a compound of intermediate composition, having the formula $C_{12}H_{12}O_2 = C_3H_3O + C_9H_9O$.

The production of amylovinic ether, $C_{14}H_{16}O_2 = C_4H_5O + C_{10}H_{11}O$, by the distillation of a mixture of the vinic and amylic alcohols with sulphuric acid, appears to be an example of the same kind of action.

It is well known that the elements themselves generally exhibit a greater tendency to renewed combination at the moment of their liberation in a free state from previous combination, or in their *nascent* state as it is termed, than in their ordinary condition; from the examples above cited this would appear to be also true of compound bodies.

When acetone and alcohol are separately saturated with hydrochloric acid gas, there is formed from the one, chloride of mesityl, C_6H_5Cl; from the other, chloride of ethyl, C_4H_5Cl; the reaction in both cases being apparently quite similar. It appeared, therefore, interesting to try the action of dry hydrochloric acid gas upon a mixture of the two.

For this purpose, a mixture of two parts by measure of alcohol and one part of acetone was treated with dry hydrochloric acid gas until nearly saturated in the cold. The spirit used contained about 91 per cent. of absolute alcohol, the acetone about 95 per cent. of real acetone; both were obtained of this strength by treating the commercial articles with carbonate of potash. The temperature of the mixture during the earlier part of the operation was allowed to rise in order to promote combination, but was suppressed during the latter part to effect a more complete saturation with the acid. During the operation, the mixture assumes a deeper colour, and ultimately becomes nearly black. On adding water to a small portion, after saturation, a very small quantity of a black oily body is thrown to the surface. By allowing the saturated mixture to remain at rest for eight or nine days, the quantity of this product is greatly increased. It may then be best eliminated by adding to the mixture four or five times its volume of water, when the insoluble crude black product rises to the surface; the quantity of this was, in one of the most successful operations, nearly equal to one-fourth of the volume of acetone

and alcohol taken. The product is not increased by allowing the mixture to remain more than eight or nine days after saturation, whilst the black tarry matter with which it is at all times contaminated, is then much increased, and the oil is rendered much more difficult to wash, owing to an increase of its specific gravity, which is then almost identical with that of water.

An attempt was made to distil the crude product, after drying and freeing it from acid by agitation with carbonate of potash; but decomposition took place, hydrochloric acid being copiously evolved. After many attempts to purify it, which were attended with only partial success, I ultimately succeeded in effecting its separation from the black tarry substance, by placing the crude product in a retort capable of holding four or five times its volume, connecting the retort with a Liebig's condenser, and passing a strong jet of steam into it through the tubulure of the retort; a pale yellow oil then passed over with the vapour of water, the quantity of the oil being somewhat greater than that of the water which accompanied it. After a second distillation by this process, the oil was obtained perfectly free from the tarry substance, but considerably diminished in volume, both from the abstraction of this tarry residue, and from the fact that a considerable quantity of acetone and alcohol was dissolved out by the steam.

The light yellow oil thus obtained was submitted to fractional distillation; complete ebullition commenced at about 100° C.; the distillation was carried on till the thermometer rose to 180°, with a considerable residue. The temperature rose gradually, but was somewhat steady between 130° and 140°. At about 140°, slight decomposition began to occur, and the contents of the retort assumed a reddish tinge, which gradually increased, the residue being nearly black. Fractions were first taken for every ten degrees.

After repeated distillations of the lower fractions, and addition of water to those portions which came over below 120° (in which they were found to be partially soluble), the range of temperature was reduced to 125° and 150°; of this, about one-half came over between 129° and 133°. About a third of the whole product distilled at a temperature above 160°, with partial decomposition, giving off hydrochloric acid. The liquid collected above 160°, when treated with alcoholic solution of potash, is instantly decomposed, with formation of chloride of potassium; with alcoholic solution of ammonia, this decomposition is much slower.

From the principal of the lower fractions (that collected between 129° and 133°) no chloride of potassium was deposited on treatment

with an alcoholic solution of potash. This portion, when treated with ordinary nitric acid, is, with the aid of gentle heat, violently acted on, with formation of an oily viscid liquid heavier than water, doubtless a nitro-compound of the original substance.

It is evident that the action of hydrochloric acid upon a mixture of acetone and alcohol leads to the formation of at least two bodies, one having its boiling point about 129° and 133°, and apparently containing no chlorine; the second having its boiling point probably considerably above 160°, which contains chlorine, and is of an extremely unstable character. I could discover no available means of isolating the latter: the study of the products of decomposition, when acted on by caustic potash, may perhaps throw some light on its constitution. Of the first, although it was many times distilled, and although the relative volumes of the different fractions were not greatly changed after each complete distillation of the whole, I could not obtain a perfectly fixed boiling point with the small quantity at my disposal.

It may be worthy of remark that the moderate action of sulphuric acid upon acetone gives rise to the formation of an oily liquid closely resembling that produced by the action of hydrochloric acid upon a mixture of acetone and alcohol. When equal volumes of acetone and concentrated sulphuric acid are carefully mixed, the acetone being added to the acid in quantities not exceeding one-hundredth part of the volume of the acid at a time, the whole rapidly shaken up and allowed to cool before the next addition, the mixture allowed to remain at rest for twenty-four hours, and then neutralised with lime, there is formed, in addition to a soluble lime-salt, an aromatic volatile oil, which may be separated by distilling the filtrate from the sulphate of lime, until about a sixth part has passed over, the oily liquid coming over first, and forming a stratum upon the surface of the aqueous distillate. The fractional distillation of this liquid after drying shows that it contains a considerable quantity of acetone; but after treating the lower fractions with water, to remove the acetone, the boiling point is considerably raised, and the range of temperature reduced to 118°—150° C. By far the largest fractions were those collected at 128°—130° and 130°—132°, the latter the greater of the two. The true boiling point is evidently about 130°—132°.

This oily liquid appears to be identical in boiling point with one of those obtained by the action of hydrochloric acid; it resembles the latter also in its insolubility in water, ready solubility in alcohol and ether, in the perfect identity of its odour (resembling that of peppermint),

and in colour. Nitric acid acts on both under the same circumstances, leading in both cases to the production of a heavy oily liquid. Indeed, there is no examined property by which they can be distinguished. The temperature at which the oily liquid is formed is very low, never more than momentarily exceeding 120° F., and never in any case, I believe, exceeding 200° F. I think the two liquids will be found to be identical; if so, this would prove that the alcohol took no part in the formation of that obtained by the action of hydrochloric acid.

NOTICES

OF

PAPERS CONTAINED IN OTHER JOURNALS.

By Henry Watts, B.A., F.C.S.

Magnus's Gas Apparatus for Organic Analysis.*

An apparatus for the purpose mentioned has been described by Dr. Sonnenschein in the "Journal für praktische Chemie," Bd. lv. 480, over which, however, the following one appears to possess some advantages. Fig. 1 (*see* p. 251) represents a front view, and Fig. 2 a side view of the apparatus.

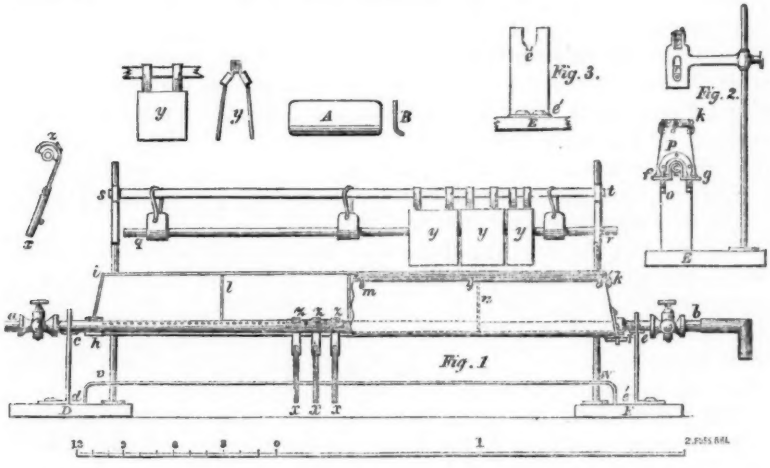
a b is a tube of brass, into which the gas is introduced by means of the two cocks *a* and *b*. This tube rests on two metal stands, *c d* and *e e'*, which are screwed into the pieces of wood *D* and *E*, and are represented, as looked at from the side, in Fig. 3. The gas issues from the tube through one hundred and eighty fine orifices, which are two lines apart from each other, and run parallel to the axis of the tube. To cause the apertures always to face upwards, the tube is furnished at *e* with a square projection, which fits into the slot *e* of the stand. At *f* and *h*, plates of brass, of the form *f g*, Fig. 2, are fastened to the tube *a b*. On these rests the chimney-like, tapering chest *f g h i k*, formed of black sheet iron, and in which the gas mixes with atmospheric air. The chest is closed above at *i k* by metallic gauze, which, in order to permit of its easy renewal, is rolled round two suitably fixed iron bars. This chest is furnished with several stays, *l m n*, which serve to impart to it a greater degree of stability. Pieces of strong wire, *o p*, are also riveted to the ends of the chest, and the extremities of these wires reach through the pieces of brass, *f*, *g*, and *h*, being held fast by small wedges. Without this precaution, the chest would rise at one or the other of its corners on heat being imparted to it, and the wire gauze would not remain plane.

q r represents the heated glass tube, which is suspended from the iron rod *s t*. From this rod the sheets of tin, *y*, are also suspended, which serve to prevent cooling by the external air.

* Communicated by H. Bence Jones, M.D.

In order to be able to heat the tube *q r* gradually from one end to the other, or to impart heat to it at particular points, the pieces of brass *x z* are made use of, by means of which the apertures of the tube *a b* may be partially closed. They are carefully grooved on to the tube *a b*, and furnished with a handle *x*, by which they can be laid upon the tube or raised off it with facility. When the pieces are laid on, the whole of the handles lean against the strong wire *v w*, which also serves to keep the pieces *D E* at a constant distance from each other. To limit the point to which the combustion is required to extend, pieces of sheet iron of the form of *A B* are laid upon the metal gauze *i k*. These pieces being gradually laid on from *k* to *i*, and the pieces *x z* being removed, the heating proceeds gradually in the same direction.

Instead of the pieces of brass *x z*, pieces of tube, capable of being turned round *a b*, and furnished with a single slit for the escape of the gas, might be made use of. The pieces *x z* appear, however, on many accounts, to be more convenient.



On the occurrence of Ozone and Peroxide of Hydrogen in the Electrolysis of Sulphuric Acid.

By Heinrich Meidinger.*

In an investigation which I undertook last summer with the view of ascertaining the causes which give rise to irregularities in the formation of the decomposition-products of water in voltametric

* Communicated by the author.

measurements, I had occasion to make some interesting observations on the relations which exist between the volume of oxygen evolved and the occurrence of ozone. It has long been recognised in a general way, that the odour which betrays the presence of this remarkable substance, is chiefly produced at low temperatures and under the influence of powerful currents, although considerable influence is likewise exerted by the strength of the acid in which the decomposition takes place, and the size of the pole from which the oxygen escapes. Now my observations show that whenever ozone is produced in considerable quantity, the volume of the evolved oxygen is much less than that which would correspond with the hydrogen given off at the same time. I will mention a few of my experiments. With a feeble current which evolved 256 cub. cents. of hydrogen in twenty-seven minutes, the quantity of oxygen obtained in that interval was almost exactly 128 cub. cents. The odour of ozone in the latter was very slight. But with a current which, in forty-six minutes, yielded 258 cub. cents. hydrogen, the quantity of oxygen obtained was only 108 cub. cents., and an insupportable odour of ozone was evolved. Similar results were obtained by varying the temperature, while the strength of the currents remained the same. Thus in one experiment, at 4° C., 227 cub. cents. hydrogen were obtained in five minutes, and only 92 cub. cents. oxygen; whereas, at 35° C., the quantities of gas evolved in the same time were 229 cub. cents. hydrogen, and 111 cub. cents. oxygen. At 67° C., the gases were evolved in the atomic proportion, and the odour of ozone was scarcely perceptible, whereas in the first experiments it was very powerful.

Variation in the strength of the acid likewise influenced the results. When the specific gravity of the acid was 1·4, there were obtained in six minutes 245 cub. cents. hydrogen, and only 87 cub. cents. oxygen; but with an acid of 1·07 spec. grav. the quantities evolved in the same time were 244 cub. cents. hydrogen, and 121 cub. cents. oxygen. Here again the oxygen smelt but very faintly of ozone.

These differences, however, become much more remarkable when, instead of the pole used in the foregoing experiments, which consisted of a piece of platinum foil 40 mm. long and 33 mm. broad, a platinum wire was used as the positive pole. Thus, with the platinum foil above mentioned, the quantities of gas evolved in nineteen minutes were 248 cub. cents. hydrogen and 122 cub. cents. oxygen; whereas with a platinum wire 20 mm. long and ½ mm. thick, the quantities obtained under exactly the same circumstances were 253 cub. cents. hydrogen, and only 40 cub. cents. oxygen,—an astonishing deficiency; and, as before, the oxygen smelt most intensely of ozone.

These experiments seem to show that the production of ozone exerts a very important influence on the volume-relations of the evolved oxygen. If now all the oxygen which was deficient in the results of the electrolysis were actually consumed in the formation of

ozone, it would follow that the ozone must be a highly condensed gas; and on the application of heat, which, as is well known, destroys the characteristic odour of ozone, the oxygen would again be set at liberty. Nevertheless, I was unable to perceive the slightest change of volume in this experiment, even when the electrolysis had taken place under the conditions in which the loss of oxygen is greatest. Moreover, I soon convinced myself, as others have likewise observed, that, notwithstanding the intense odour, the quantity of ozone present is always very small; for, on destroying it by means of iodide of potassium, the diminution of volume produced was only $\frac{1}{300}$.

Hence it follows that the large quantity of oxygen which had disappeared during the electrolysis must be contained in the electrolyte itself, and either as ozone, or as some higher oxide of hydrogen, —most probably HO_2. In fact, iodide of potassium assumed a very deep brown colour, when mixed with only a single drop of the liquid. As, however, this liquid exhibited not the slightest odour of ozone, the reaction could be attributed to nothing but the presence of binoxide of hydrogen, the acid at the same time exhibiting all the characters which Thénard ascribes to that compound: *e. g.* A piece of very pure platinum, or the pole itself, caused a continuous evolution of gas-bubbles, which by analysis were found to consist of pure oxygen; the same gas was obtained in large quantity on heating the liquid.

The formation of peroxide of hydrogen in the electrolysis of sulphuric acid being thus established, it became interesting to inquire whether this reaction could be made the basis of a practical mode of preparing the peroxide. I found that the acid in which its formation was most abundant had a specific gravity of 1·4. With regard to the temperature of the acid during the decomposition, I may state, as a general rule, that it should be kept as low as possible. It might indeed be possible, by lowering the temperature sufficiently, to cause the oxygen to disappear entirely, and obtain pure ozone. I likewise endeavoured to determine the best dimensions for the pole. I found that with a current which at 18° C. and 335″ bar. evolves 67 cub. cents. of hydrogen in ten minutes (such a current as may generally be obtained with three of Bunsen's cells), the best size for the pole is 10 mm. of wire 0·5 mm. thick. When a still smaller wire was taken, the quantity of oxygen evolved became greater, because the pole was very strongly heated in consequence of the resistance which it presented to the escape of the electricity, and thereby prevented the more abundant formation of peroxide of hydrogen. The absolute strength of the current, as shown by the quantity of hydrogen evolved, has no influence whatever on the formation of peroxide of hydrogen; the essential condition to be fulfilled is to increase the intensity of the escaping electricity as much as possible at the point of evolution. This end is attained by the use of a very small platinum pole. The most favourable size of the pole for a current of given

strength has already been mentioned; for a current of double strength the pole must have a double surface; in a word, to obtain the greatest possible formation of peroxide of hydrogen, the strength of the current and the size of the pole must be made to vary in the same ratio. Under the circumstances above detailed, at a medium summer temperature of 20° C., and with a power of three Bunsen's cells, 300 cub. cents. of oxygen were converted into peroxide of hydrogen in two hours,—a rate of production which in a day of twenty-four hours would yield nearly eleven grammes of peroxide of hydrogen.

It can scarcely be doubted that the presence of peroxide of hydrogen in the decomposition-cell must exert considerable influence on the quantity of hydrogen evolved in electrolysis. I have proved, indeed, by several comparative experiments, in which two voltameters were introduced into the same circuit—the one filled with pure sulphuric acid, the other with acid which had been frequently used for decomposition—that the quantity of hydrogen evolved in the latter is much less than in the former, especially when large plates are used for the poles. It may therefore be laid down as a rule in voltametric measurements, to use as pure an acid as possible, or, if it has been already used, to free it from peroxide of hydrogen by long boiling, introducing a piece of platinum to facilitate the decomposition, and further to evolve the hydrogen from small poles consisting of platinum wires. As to the formation of oxygen, it is best, in most cases, not to place any dependence upon it for purposes of measurement, inasmuch as the production of peroxide of hydrogen cannot in any case be completely avoided.* If, however, it be desired to collect the two gases in equivalent proportions, it is best to use a comparatively weak acid, of specific gravity about 1·1, and to evolve the hydrogen on a wire, the oxygen on a platinum plate of not too small dimensions.

Since the appearance of the larger memoir, from which the present is an extract, in "Liebig's Annalen,"† MM. Jamin and Leblanc have published in the "Comptes rendus" a number of experiments relating to the same subject. These experimenters have likewise observed the formation of peroxide of hydrogen, without, as it appears, being acquainted with my former experiments. I wish, therefore, to observe that I showed the facts above mentioned, in the course of last summer, to several physicists, viz. to Professors Buff and Kopp in Giessen, and Dr. Hofmann in London.

In another memoir, Jamin communicates the observation that

* The formation of this compound was observed even in distilled water decomposed by a battery of 44 Bunsen's cells, also in highly concentrated sulphuric acid; it even took place when a small platinum wire was used as the positive pole, in the decomposition of an acid whose temperature was much above the boiling point of water. In all these cases, the simultaneous production of ozone was demonstrated both by the odour and by its reaction on starch-paste mixed with iodide of potassium.

† Ann. Ch. Pharm. lxxxviii. 57.

hydrogen evolved by electrolytic action sometimes possesses the property of being partially absorbed by pure platinum; and that a larger quantity of electricity—that is to say, a stronger current—is required to evolve a given volume of this hydrogen, than to obtain an equal volume of ordinary non-absorbable hydrogen. According to Jamin's view, this effect is to be attributed to a peculiar modification of hydrogen which that substance, like oxygen, undergoes during electrolysis, or to a peculiarity in the current, by which, contrary to the ordinary supposition, oxygen is subsequently evolved at the pole which had previously yielded hydrogen; and this oxygen, in contact with platinum, causes the absorption of the hydrogen.

I will mention one of the experiments which I have made upon this subject. I placed two voltameters in the same circuit, one of them (*A*) containing pure acid, quite free from peroxide of hydrogen, the other (*B*) filled with an acid very rich in that compound. In both voltameters, the hydrogen was evolved on small platinum wires of equal dimensions. In *A*, I obtained in half an hour 242 cub. cents. hydrogen; but in *B* only 218 cub. cents. When now the two bell-jars in which the hydrogen had been received were carefully removed from the acid, placed in pure water, and a platinum wire, previously ignited by a spirit lamp, introduced into each, the volume of *A* was found not to vary for several days, while that of *B* diminished in the same time to 206 cub. cents. The explanation of this phenomenon is perhaps simply the following: The peroxide of hydrogen in the cell *B* oxidised part of the hydrogen *in statu nascenti;* hence only 218 cub. cents. of gas were obtained in that cell, while in *A* the quantity amounted to 242 cub. cents. Consequently, to eliminate a given volume of hydrogen, a greater quantity of electricity would be required in *B* than in *A*. But the agitation caused by the ascending gas-bubbles, and the rise of temperature accompanying the electrolysis, likewise give rise to a spontaneous decomposition of the peroxide of hydrogen, and a liberation of oxygen, which is thereby compelled to ascend into the same bell-jar with the hydrogen. In this experiment, the quantity of oxygen thus set free by the decomposition of the peroxide of hydrogen amounted to 4 cub. cents.; this quantity combined at the surface of the platinum with 8 cub. cents. of hydrogen; so that, in all, the volume of this gas was diminished by 12 cub. cents. This reaction is not always so striking as in the case just adduced, but when I used sulphuric acid perfectly free from peroxide of hydrogen, I could never perceive any such absorption of the hydrogen.

New Researches on the Metals accompanying Platinum in the Ore.*

By E. Fremy.

Platinum-residues may be divided, according to their composition, into three classes:

1. The *pulverulent residue* is a mixture of iridium and rhodium; it is derived from the acid solutions which have been precipitated by iron, and retains but small quantities of osmium: the metals composing this residue have been dissolved in aqua-regia through the medium of bichloride of platinum.

2. The *scaly residue*, known to all chemists, and distinguished by the improper name of *Osmide of Iridium*, is a quaternary alloy of iridium, ruthenium, rhodium, and osmium: the rhodium occurs in these scales in small quantity only.

3. The third residue, which may be called the *granular residue*, consists essentially of rhodium, osmium, and iridium.

To obtain rhodium, therefore, we may operate on the pulverulent or the granular residue; either of the three residues may be used for the preparation of iridium; the scaly residues are the only ones from which ruthenium can be conveniently prepared; and osmium must be extracted principally from the granular and scaly residues.

The following methods of treating these residues depend partly on the great fixity of oxide of ruthenium, and partly on the striking analogies between osmium and arsenic. Take, for example, the scaly residue.

Oxide of ruthenium being able to bear a red heat without decomposing, and osmium being actually roasted by the action of oxygen, producing a volatile acid, just as sulphur and arsenic do, the residue of platinum-ore may be decomposed by roasting, like metallic sulphides and arsenides. By submitting it to this operation, osmic acid is produced in large quantity, and very pure; and oxide of ruthenium is obtained in well-defined crystals,—a state in which it has hitherto not been known.

The following is a description of the apparatus for roasting platinum-residues, which has long been in use in the author's laboratory, and is now fitted up in the platinum works of MM. Demontis and Chapuis, and will furnish chemists with a variety of useful and interesting products hitherto little known.

The roasting is performed by means of atmospheric air, previously freed from organic matter by passing through a tube filled with pumice stone impregnated with sulphuric acid. The platinum-residue is heated to redness, and placed in a tube of earthenware, or better of platinum; and the air is drawn into the apparatus by means of an

* Compt. rend. xxxviii. 1008.

ordinary aspirator. The tube communicates with a series of glass flasks, in which the osmic acid condenses, and likewise contains, in the part which projects from the furnace and communicates with the flasks, a few fragments of porcelain, which during the operation become covered with beautiful crystals of oxide of ruthenium, which is not volatile, but is carried forward by the vapours of osmic acid. The atmospheric air which has traversed the flasks and is saturated with osmic acid vapour, is conducted into a solution of potash, and finally passes into the aspirator. The osmiate of potash thus formed is treated with a fews drops of alcohol, and thereby brought to the state of osmite of potash, crystallised, and insoluble in water containing alcohol.

This roasting presents no difficulty, and yields the following products:—1. Osmic acid very pure, and in quantity sometimes exceeding 40 per cent. of the platinum-residue used.—2. Osmite of potash, from which metallic osmium and its derivatives may be readily prepared by a method described in a preceding memoir.—3. Crystallised oxide of ruthenium.—4. An alloy of iridium and rhodium, which remains in the roasting tube.

The operation just described is important, not only for the preparation of bodies like osmic acid and oxide of ruthenium, which hitherto were very difficult to obtain, but it likewise serves in a manner to complete the history of osmium, by showing that this body differs completely in all its properties from the accompanying platinum-metals, and appears to play the same part in the ore that arsenic plays in the metallic arsenides.

It may be safely predicted that osmium will be found to combine with hydrogen, and, like arsenic and phosphorus, to enter into organic molecules and form compounds similar to those of arsenic, phosphorus, &c., lately discovered. The author has made some researches in this direction, which will be published hereafter.

By submitting the osmiates to the action of oxygen and oxidising agents, an acid is formed containing more oxygen than osmic acid; and if, as some analyses seem to show, the formula of this acid is $Os O_5$, the oxidation-series of osmium will be—

$$Os O;\ Os_2 O_3;\ Os O_2;\ Os O_3;\ Os O_4;\ Os O_5:—$$

presenting remarkable analogies to those of nitrogen, phosphorus, and arsenic.

The new acid is very unstable; it forms with potash and soda, salts which have a dark brown colour, and sometimes crystallise in the alkaline liquids.

It has been already stated, that the roasting of the platinum-residue leaves as a fixed product, an alloy of iridium and rhodium; the alloy is often mixed with oxide of ruthenium not carried forward by the osmic acid vapour, and likewise retains traces of osmium.

The oxide of ruthenium is first separated by heating the residue with fused potash, which dissolves the metallic oxide, after which the iridium is separated from the rhodium by the following method, differing but little from that recommended by Wöhler.

The alloy is heated with four parts of nitre; the mass digested in boiling water, which often, on cooling, deposits fine octohedral crystals of osmite of potash; and the residue treated with aqua-regia, which converts the iridium into chloride. This body then combines with the chloride of potassium, forming a double salt, which dissolves in boiling water, and crystallises on cooling. The insoluble residue is mixed with common salt, and exposed at a dull red heat to a current of dry chlorine; a double chloride of sodium and rhodium is then formed, which is soluble in water, and is deposited from its solutions in violet octohedral crystals, often of considerable size. The easy preparation of rhodium-salts by the preceding process will enable us to complete the history of this metal, which recomends itself to the attention of chemists by its insolubility in aqua-regia, its lustre, which is nearly equal to that of silver; the beauty of its crystalline compounds; and, above all, by its analogies with platinum and iridium. The author has already ascertained that the salts of rhodium, when subjected to the action of ammonia, form a class of ammonio-rhodic salts, which crystallise readily, like the corresponding salts of platinum, palladium, and iridium.

All these facts will be more fully developed in a future communication.

Arsenides of Ethyl, or Arsenethyls.*

By Hans Landolt.

These compounds are obtained by the action of iodide of ethyl on arsenide of sodium. They are three in number, viz.:—arsenbiethyl or vino-cacodyl, $(C_4 H_5)_2$, As; arsentriethyl, $(C_4 H_5)_3$ As; and arsenethylium, $(C_4 H_5)_4$ As. This last is analogous to tetrethylium, stibmethylium, &c.

Preparation.—1. Arsenide of sodium, prepared by the direct combination of its elements,† is finely pounded together with four or five times its weight of quartz-sand (if pulverised alone, it takes fire), and the mixture introduced into a number of small short-necked flasks

* Ann. Pharm. lxxxix. 301; Chem. Gaz. 1854.

† Pure metallic arsenic, in the state of fine powder, is gently heated in a furnace having a good draught, till it begins to fume, and small pieces of sodium introduced from time to time, till the mixture begins to assume a fluid consistence, which effect takes place when a quantity of sodium has been introduced, about equal to that of the arsenic. As the product is highly combustible, it is necessary to exclude the air as completely as possible during the whole operation. For this purpose, the arsenic is placed in a porcelain crucible, enclosed within a Hessian crucible, both being

(holding about 3 oz.), so as to fill them to about two-thirds. Iodide of ethyl is then added to the contents of one of the flasks (the others being well corked up), and the flask immediately connected with a condensing apparatus (the same as that used by Löwig and Schweitzer in the preparation of stibethyl), consisting of a tall wide cylindrical vessel closed by a cork having three apertures. Through one of these apertures passes a tube, proceeding from the carbonic acid apparatus, and reaching to the bottom of the vessel; through the second, a short straight tube, to carry that gas off; and through the third is inserted the distillation-tube, connected with the flask containing the mixture. Within the glass cylinder are placed two small bottles, into one of which the lower end of this conducting-tube is inserted. The mixture of iodide of ethyl and arsenide of sodium soon becomes so hot that a large portion of the iodide of ethyl distils over spontaneously; as soon as the action is over, the flask is removed, more iodide of ethyl poured in, and the same operation repeated as long as any action takes place. The final residue of iodide of ethyl is expelled by gently heating the flask; and on subsequently applying a stronger heat, the arsenides of ethyl distil over. The cork of the cylindrical vessel must then be raised, together with the tubes, the vessel turned round so as to bring the end of the distillation-tube over the second bottle, and the vessel again closed as before. The exact moment for changing the bottles may be known by the conducting-tube, which has previously been hot and dry, becoming cold and wetted with drops of liquid. The heat is then gradually raised to redness; and when nothing more passes over, the flask is removed, a second put in its place, and the whole series of operations repeated. The contents of twelve or fifteen flasks (requiring about a pound of iodide of ethyl) yield about two ounces of the mixed arsenides of ethyl.—At the end of the operation the first bottle contains iodide of ethyl mixed with a small quantity of the arsenides; the second, a nearly colourless liquid, frequently mixed with a red substance. This liquid—which is heavier than water, has an intolerable odour, excites a copious flow of tears, fumes strongly in the air, and afterwards takes fire—is a mixture of arsenbiethyl and arsentriethyl. These two compounds may be separated by fractional distillation, the latter being much the more volatile of the two. For this purpose the crude product is transferred, within an atmosphere of carbonic acid, into a small flask, and the flask immediately connected with the distillation-tube of the condensing apparatus above described, a

provided with closely fitting covers, which must only be removed to introduce the sodium, or to stir the mixture with an iron rod, so as to ensure uniform combination. The action is very violent, and attended with vivid incandescence, portions of the mixture being sometimes thrown out. The alloy, which has a crystalline fracture and silver-white colour, must be kept in closely-stoppered bottles filled up with quartz-sand. It decomposes water, with evolution of arseniuretted hydrogen,—an effect which takes place even in damp air; hence it must be handled with caution.

number of small bottles being previously arranged within the large cylindrical vessel, so that by turning the vessel, each of them may be successively brought beneath the extremity of the distillation-tube. The flask is heated in a small sand-bath, and a rapid current of carbonic acid gas passed through the apparatus during the whole operation. This process is best adapted for the preparation of arsentriethyl, which it yields in much larger quantity than arsenbiethyl. The latter is more advantageously obtained by the following process:

2. Arsenide of sodium is heated with excess of iodide of ethyl, as before; the product digested with ether; the ethereal extract (which contains arsenbiethyl, arsentriethyl, and iodide of ethyl) mixed with absolute alcohol; the ether distilled off; and the alcoholic solution mixed with water, which precipitates arsenbiethyl and dissolves iodide of arsenethylium, formed by the action of the iodide of ethyl on arsentriethyl. The treatment of the arsenide of sodium with iodide of ethyl is performed in small flasks, as in the first process, and the iodide of ethyl, which distils over in consequence of the heat generated by the reaction, is collected in a small flask, and subsequently poured back again, together with fresh iodide of ethyl, these operations being repeated as long as any action continues: the transference of the liquid must be effected as quickly as possible, to avoid access of air. When the action is over, the greater part of the remaining iodide of ethyl must be distilled off by a gentle heat,—sufficient, however, being left to keep the mixture moist; if the excess were all removed, the final product would consist of a mixture of arsenbiethyl and arsentriethyl, which would then require fractional distillation to separate them. When the contents of ten or twelve flasks have been thus treated, the whole is transferred into a bottle containing from one and a half to two pounds of ether, and previously filled with carbonic acid; the bottle tightly closed and well shaken; the contents left to stand till the liquid has become clear; this liquid decanted into another bottle filled with carbonic acid (whereupon it generally becomes turbid and deposits a yellow powder, the quantity of which is greater the longer the liquid has been exposed to the air during the several operations); the residue again treated with ether; and this treatment repeated as long as a drop of the ethereal extract becomes turbid on exposure to the air. The whole of the ethereal extract is then mixed with absolute alcohol, and the ether quickly distilled off. During the distillation, the yellow powder just mentioned cakes together and forms a red resinous body, melting at 70°, and insoluble in all reagents.

The alcoholic solution is next transferred, in an atmosphere of carbonic acid, into a cylindrical glass vessel, capable of being well closed, and mixed with water free from air till it becomes very turbid. It is left to stand till it becomes clear and an oily body separates out, then decanted from this oil to another vessel, and a

large quantity of water added; whereupon arsenbiethyl is separated in the form of an oily liquid having a faint greenish-yellow colour and powerful odour. It is decanted into a small bottle, freed from the supernatant liquid by means of a pipette, and preserved under a layer of de-aërated water. In all these operations the greatest care must be taken to exclude the air; otherwise a red powder forms, which mixes with the radical, and renders its purification very difficult.

The water used for precipitating the arsenbiethyl contains iodide of arsenethylium, together with other arsenical compounds, which have not yet been separated one from the other. On agitating the watery liquid with ether, a portion of these compounds dissolves, together with a considerable quantity of iodide of arsenethylium, although this compound is by itself but sparingly soluble in ether; and on leaving the liquid to evaporate in the air, there remains a yellow syrup, from which, after a while, the iodide of arsenethylium separates in beautiful prismatic crystals. It may be separated from the liquid compounds which adhere to it, by washing with a small quantity of water, and obtained in a state of purity by several recrystallisations from water. The watery solution, after being heated with ether as above, still contains a small quantity of iodide of arsenethylium, which may be crystallised by evaporation over the water-bath; but it is very impure.

The residue in the flasks in which arsenide of sodium has been treated with iodide of ethyl, and the product digested with ether (p. 260), still contains a number of arsenical organic compounds, among which the oxide of arsentriethyl, $Ae_3\,As\,O_2$, exists in considerable quantity. It may be separated by treating the residue with absolute alcohol, evaporating the alcoholic extract, and subjecting it to dry distillation; the oxide then passes over in the form of a yellow liquid.

Arsenbiethyl, or *Vinocacodyl*, $(C_4\,H_5)_2\,As$.

For the preparation, *vide* p. 260.

Properties.—Oily liquid, having a faint yellowish colour, strong refracting power, and a very disagreeable, pungent, alliaceous odour. Heavier than water, in which it sinks without mixing. Boils between 185° and 190°.

		Calculation.	Experiment (mean).
8 C . . .	48	36·09	35·73
10 H . . .	10	7·52	7·75
As . . .	75	56·39	56·92
$(C_4\,H_5)_2\,As$ . .	133	100·00	

Arsenbiethyl rapidly absorbs oxygen from the air, and generally breaks out into a dull flame, giving off vapours of arsenious acid.

In this respect, however, its properties vary according to the mode of preparation. A drop of the product obtained by the first method (p. 259) takes fire immediately when let fall upon wood or paper; but with that which is obtained by the second method (p. 260) this effect does not take place till the temperature is raised to 180°. Strong nitric acid oxidises it rapidly, with evolution of light and heat. Dilute nitric acid likewise oxidises it, but less completely, a red substance analogous to Bunsen's *erythrarsin* being formed as a secondary product. This red body, which is likewise formed when arsenbiethyl is incompletely burned in the air, is light red when first produced, but soon becomes darker, and when dry forms a brown powder, which turns white by continued exposure to the air: it is insoluble in water, alcohol, and ether; heated on platinum-foil, it burns away completely, with a pale arsenic flame; heated in a test-tube, it gives off inflammable vapours having an unpleasant odour, and leaves a considerable quantity of arsenic. Strong sulphuric acid has no action on arsenbiethyl at ordinary temperatures, but evolves sulphurous acid when heated with it; dilute sulphuric acid does not affect it. Arsenbiethyl reduces the noble metals from their solutions; its alcoholic solution, added to a solution of nitrate of silver or corrosive sublimate, immediately throws down metallic silver or mercury. This character, and the production of the red powder above mentioned, distinguish arsenbiethyl from the other arsenides of ethyl.

Combinations.—Arsenbiethyl combines directly with sulphur and with the halogen-radicals, the combination being attended with great evolution of heat. All its compounds hitherto obtained are liquid, and distinguished by a peculiarly repulsive and persistent odour, which excites a copious flow of tears: continued exposure to this odour produces sneezing, persistent catarrh, and headache. The compounds contain 1 at. arsenbiethyl, with 1 at. O, S, Cl, &c.

Iodide of Arsenbiethyl.—Obtained by saturating an ethereal solution of arsenbiethyl with an ethereal solution of iodine, and evaporating the mixture out of contact of air. Yellow oil, readily soluble in alcohol and ether, but not miscible with water. Does not fume in the air, but burns slowly when heated, giving off vapours of iodine. Decomposed by sulphuric and nitric acids, with separation of iodine. The alcoholic solution, mixed with nitrate of silver, forms an immediate precipitate of iodide of silver, but gives no precipitate with a solution of corrosive sublimate in dilute alcohol.

		Calculation.	Experiment.
8 C	48	18·53	18·90 to 19·34
10 H	10	3·86	4·13 „ 4·73
As	75	28·96	— —
I	126	48·65	48·45 „ 49·13
$(C_4H_5)_2AsI$.	259	100·00	

Arsenbiethyl is insoluble in water, but dissolves readily in alcohol and ether, and is precipitated from its alcoholic solution by water.

Arsentriethyl, $(C_4 H_5)_3 As$.

This compound is most advantageously obtained by the first method (p. 259); it passes over in a state of purity between 140° and 180°.

Properties.—Colourless, very mobile liquid, having great refracting power, and a disagreeable odour, like that of arseniuretted hydrogen gas. Sp. gr. 1·151 at 16°·7. Under a pressure of 736 mm. it begins to boil at 140°; but the boiling point slowly rises to 180°, a small quantity of metallic arsenic separating at the same time. Hence the compound appears to decompose in boiling. The quantity thus decomposed is, however, very small, several portions collected between 140° and 170° not exhibiting a difference of more than 1 per cent. in the amount of carbon. Vapour density 5·2783.

	Calculation.		Experiment.
12 C . . .	72	44·44	43·21 to 44·03
15 H . . .	15	9·26	9·41 „ 9·88
As . . .	75	46·30	— —
$(C_4 H_5)_3 As$ . .	162	100·00	

Decompositions.—Arsentriethyl fumes and becomes hot when exposed to the air, but seldom takes fire unless it is gently heated from without; the products of the combustion are arsenious acid, carbonic acid, and water. Oxidation takes place slowly, even when the compound is kept under water in a tightly-closed vessel; when it has advanced a certain stage, the liquid no longer fumes in the air. Strong nitric acid oxidises it rapidly, with vivid combustion and explosion; but nitric acid of sp. gr. 1·42 dissolves it slowly, with evolution of nitric oxide, and forms nitrate of arsentriethyl; no red compound analogous to erythrarsin is formed, either by the action of nitric acid or by oxidation in the air. Arsentriethyl mixes with oil of vitriol, and on the application of heat reduces it to sulphurous acid. It does not reduce the oxides of the noble metals.

Combinations.—Arsentriethyl combines with oxygen, sulphur, chlorine, &c., forming compounds containing 1 at. of the radical, and 2 at. of the other body,—analogous, therefore, to the compounds of stibmethyl, stibethyl, &c.

Oxide.—When an ethereal solution of pure arsentriethyl is left to evaporate slowly in contact with the air at ordinary temperatures, the oxide remains in the form of a nearly colourless oily liquid, having a slight alliaceous odour. As thus obtained, however, it is not pure, being mixed with other compounds not yet examined.

It is best prepared by exhausting the mass obtained by treating

arsenide of sodium with iodide of ethyl, first with ether, and afterwards with absolute alcohol; evaporating the alcoholic extract, and subjecting the residue to dry distillation in a retort (p. 261).

Oily liquid, having a slight yellowish colour; heavier than water, and not miscible with it; dissolves readily in alcohol and ether, and is precipitated from the alcoholic solution by water in its original state.

The alcoholic solution has no action on litmus paper, and does not precipitate nitrate of silver. The oxide is readily dissolved by dilute nitric acid, but is insoluble in dilute sulphuric and hydrochloric acids.

		Calculation.		Experiment.
12 C	. . .	72	40·45	39·58 to 40·38
15 H	. . .	15	8·43	8·73 „ 9·29
As	. . .	75	42·13	43·17 —
2 O	. . .	16	8·99	— —
$(C_4H_5)_3AsO_2$	. .	178	100·00	

This compound becomes turbid on exposure to the air, and passes to a higher state of oxidation, but without fuming or inflammation.

When pure arsentriethyl is left to stand for some time in a loosely-stoppered bottle, very fine tabular crystals gradually form on the surface; and if the crust thus formed be now and then broken and pushed to the bottom, the entire liquid may be converted into a solid compound. The crystals are quite inodorous, and dissolve in alcohol and ether; but in contact with water, they deliquesce to a colourless oil, which remains quite undissolved; deliquescence likewise takes place in a moist atmosphere, and on exposure to a gentle heat.

This compound has an acid reaction; its alcoholic solution forms with nitrate of siver a yellow flocculent precipitate which shrinks up greatly in drying, and forms a brown powder, containing 60·8 per cent. of silver.

Sulphide.—1. When an ethereal solution of arsentriethyl is boiled with washed flowers of sulphur, the liquid decanted into another vessel as soon as the excess of sulphur has settled down, and left to cool, the sulphide of arsentriethyl separates out in prismatic crystals; if, however, too much ether has been used, the crystals do not form till the liquid is evaporated. The crystals are generally contaminated both with sulphur and with oxide of arsentriethyl, which latter is very difficult to remove. They are best purified by recrystallisation from alcohol or water, the compound then separating in small feathery crystals; larger crystals may be obtained by redissolving in warm ether, and leaving the solution to evaporate slowly.

2. The compound may likewise be obtained by boiling an aqueous solution of pentasulphide of potassium with oxide of arsentriethyl;

crystals of the sulphide then separate on cooling. It has a bitter taste, but is quite inodorous when pure.

	Calculation.		Experiment.	
12 C . . .	72	37·11	—	—
15 H . . .	15	7·73	—	—
As . . .	75	38·66	—	—
2 S . . .	32	16·50	16·17 to	15·77
$(C_4H_5)_3AsS_2$ . .	194	100·00		

Sulphide of arsentriethyl is not altered by exposure to the air. Heated in a test-tube, it melts somewhat below 100°, forming a yellowish oily liquid, which boils at a higher temperature, giving off spontaneously inflammable vapours, and covering the inside of the tube with a yellowish-red deposit of sulphide of arsenic. When boiled with potash-ley, it is not decomposed, but merely melts, and solidifies in a crystalline mass on cooling. Strong nitric acid acts very powerfully on it, converting the sulphur into sulphuric acid; and partially oxidising the arsentriethyl. Dilute hydrochloric acid decomposes it imperfectly, giving off sulphuretted hydrogen, and forming a small quantity of arsentriethyl, which may be recognised by its pungent odour. The aqueous solution forms with nitrate of silver a black precipitate of sulphide of silver: no precipitate with acetate of lead, or with copper salts. With mercurous nitrate it forms a black precipitate, which soon turns white; with corrosive sublimate, a bulky white precipitate. Sulphide of arsentriethyl dissolves readily in warm water and in boiling ether, but is nearly insoluble in cold ether.

Iodide of Arsentriethyl.—When an ethereal solution of iodine is added to an ethereal solution of arsentriethyl, so long as decoloration takes place iodide of arsentriethyl separates in large quantity as a sulphur-yellow flocculent precipitate. It is immediately separated from the liquid, washed with a small quantity of ether, pressed between paper, dried at a very gentle heat, and then enclosed in a tight-stoppered bottle.—Very unstable: when exposed to the air, if only for a short time, it turns brown, and soon deliquesces to a dark-coloured syrupy liquid; even when completely protected from the air, it gradually assumes a brown colour. When heated in a test-tube, it assumes a darker colour, and at 160° fuses to a brown liquid, which solidifies again on cooling; at 190° it is converted, with partial decomposition, into vapour, which condenses on the colder parts of the tube in light yellow drops; no separation of iodine appears to take place. Nitric and sulphuric acids decompose it immediately, with separation of iodine; it dissolves in hydrochloric acid when heated, but separates out again, unchanged, on cooling. Strong potash-ley dissolves out the iodine, and forms oxide of arsentriethyl.

Iodide of arsentriethyl dissolves readily in water and alcohol, but sparingly in ether. The aqueous solution forms with nitrate of silver an immediate precipitate of iodide of silver; from acetate of lead it separates iodide of lead. With corrosive sublimate it forms a white precipitate, soluble in excess.

	Calculation.		Experiment.
12 C . . .	72	17·39	17·68
15 H . . .	15	3·62	4·14
As . . .	75	18·12	—
2 I . . .	252	60·87	60·64
$(C_4H_5)_3AsI_2$ . .	414	100·00	

Chloride.—Not yet obtained in a definite state.

When an alcoholic solution of oxide of arsentriethyl is mixed with strong hydrochloric acid, and water afterwards added, the oxide separates out unaltered; but the liquid at the same time acquires an intolerable odour, which attacks the eyes strongly: this odour is altogether foreign to the oxide of arsentriethyl, and is therefore probably due to the formation of a small quantity of chloride.

Nitrate.—Obtained by treating arsentriethyl or its oxide with dilute nitric acid. On evaporating the liquid over the water-bath, a thick syrup is obtained; this, when left for some time over sulphuric acid, deposits crystals, which, on exposure to the air, rapidly absorb water and deliquesce.

Arsenethylium, $(C_4H_5)_4As$.

Formed as an iodide, by the action of iodide of ethyl on arsentriethyl:

$$(C_4H_5)_3As + C_4H_5I = (CH_5)_4As, I.$$

Not known in the free state.

16 C . . .	96	50·26
20 H . . .	20	10·47
As . . .	75	39·27
$(C_4H_5)_4As$ . .	191	100·00

The compounds of arsenethylium are analogous to those of potassium, ammonium, tetrethylium, stibmethylium, &c. The hydrated oxide is a fixed base, resembling hydrate of potash. The salts dissolve readily in water, crystallise readily, and possess great stability, undergoing no change on exposure to the air; they are inodorous, have a bitter taste, and do not appear to be poisonous. In these respects they differ remarkably from the compounds of arsenbiethyl and arsentriethyl.

Oxide.—Obtained by the action of oxide of silver on an aqueous solution of iodide of arsenethylium. On filtering from the iodide

of silver, and evaporating the solution, the air being excluded as much as possible, the hydrated oxide remains in the form of a white mass, which has a strong alkaline reaction, and quickly absorbs water and carbonic acid from the air. It is a strong base, separating ammonia from its salts at ordinary temperatures, and precipitating the earths and the heavy metallic oxides from their solutions.

Iodide.—When iodide of ethyl is mixed with arsentriethyl, combination generally takes place in a few hours, the entire liquid solidifying in a mass of crystals. For the preparation, *vide* p. 261. Large colourless crystals, which often become somewhat darker by long keeping. They dissolve readily in water and alcohol; but are insoluble in ether, and in alcohol containing ether. Nitric acid separates iodine; so, likewise, does sulphuric acid, with evolution of hydriodic and sulphuric acids. The crystals fall to powder when heated, giving off vapours which take fire in the air, and yielding a sublimate of metallic arsenic, but only a small quantity of iodide of arsenic.

	Calculation.		Experiment.	
			a.	*b.*
16 C . . .	96	30·28	28·77	—
20 H . . .	20	6·31	6·84	—
As . . .	75	23·66	—	—
I . . .	126	39·75	39·09	39·85
$(C_4 H_5)_4$ As I . .	317	100·00		

a was obtained by method 1, p. 259; *b* by method 2, p. 262.

Chloride.—Obtained by saturating a solution of the oxide with dilute hydrochloric acid; on evaporating the liquid under the air-pump, crystals are formed containing 8 atoms of water of crystallisation, and deliquescing rapidly in the air. When heated, they first melt in their water of crystallisation, and then gradually give it off, undergoing decomposition at the same time; and ultimately disappear altogether, with formation of volatile products. Strong sulphuric acid decomposes the salt immediately, with evolution of hydrochloric acid gas. The crystals dissolve readily in water and alcohol, but are insoluble in ether. The aqueous solution immediately precipitates chloride of silver from the nitrate, and forms an insoluble double salt with protochloride of mercury.

	Calculation.		Experiment.	
16 C . . .	96·0	32·16	—	—
20 H . . .	20·0	6·70	—	—
As . .	75·0	25·13	—	—
Cl . .	35·4	11·89	11·88	11·98
8 HO . .	72·0	24·12	—	—
$(C_4 H_5)$ As Cl + 8 Aq	298·4	100·00		

Sulphate.—Obtained by precipitating iodide of arsenethylium with a solution of sulphate of silver containing excess of sulphuric acid. The liquid, when filtered and evaporated, leaves granular crystals, which may be purified by repeated crystallisation. This salt dissolves readily in water and alcohol, sparingly in ether; its taste is sour at first, afterwards bitter. Heated in a tube, it fuses with decrepitation at first, and then gives off acid vapours, which do not take fire in the air.

		Calculation.	Experiment.
16 C	96	33·33	33 05
20 H	20	6·94	7·55
As	75	26·04	—
O	8	2·78	—
2 SO	80	27·78	28·25
HO	9	3·13	—
$(C_4H_5)_4$	288	100·00	

Plumbides of Ethyl, or Plumbethyls.*

By Karl Löwig.

These compounds are formed by the action of iodide of ethyl on plumbide of sodium containing one part sodium to six parts lead. On agitating the resulting mass with ether, and evaporating the ethereal solution, there remains a mixture of several plumbides of ethyl, which have not yet been separated from one another, the separation being very difficult in consequence of the great similarity of their physical properties. These radicals are perfectly colourless, tolerably mobile, volatile, and have a powerful odour. They do not fume in the air, but when set on fire they burn and give off dense clouds of oxide of lead. When strong nitric acid is poured upon them they take fire; and in contact with iodine or bromine, especially with the latter, they explode with violence. They are insoluble in water, but dissolve readily in alcohol or ether. The ethereal or alcoholic solution, when exposed to the air, deposits an amorphous powder, which is insoluble in water, alcohol, and ether, and forms crystallisable salts with acids; and in solution there remains a strongly alkaline base, the oxide of *methylo-plumbethyl*, $(C_4H_5)_3Pb_2$, the radical of which constitutes the principal portion of the product obtained by the action of iodide of ethyl on plumbide of sodium.

* J. pr. Chem. lx. 304; Ann. Pharm. lxxviii. 318.

Oxide of Methyloplumbethyl $(C_4 H_5)_3 Pb_2 O$.—Obtained as a hydrate by adding a solution of nitrate of silver, mixed with alcohol, to the alcoholic solution of the mixed radicals, as long as metallic silver is precipitated; filtering from the silver; agitating the resulting solution of nitrate of methyloplumbethyl with alcoholic potash, and afterwards with ether; adding a sufficient quantity of water to separate the ethereal solution of the oxide, and evaporating the ether in a retort. Pure hydrated oxide of methyloplumbethyl then remains in the form of a thick oily liquid, which solidifies after a while in a crystalline mass slippery to the touch, like hydrate of potash. It is volatile, and forms white fumes when a rod moistened with hydrochloric acid is held over it. When heated, it gives off white vapours, which excite powerful sneezing,—a property which also belongs to the radical itself and to many of its compounds. The hydrate dissolves sparingly in water, readily in alcohol and in ether. The solutions have a strong alkaline reaction; a sharp, disagreeable, caustic taste; and produce an extremely unpleasant sensation in the throat.

Carbonate.—The hydrated oxide rapidly absorbs carbonic acid from the air. By leaving the alcoholic solution of the oxide to evaporate in the air, the carbonate is obtained in small hard crystals. It is nearly insoluble in water, sparingly soluble in alcohol and ether. Alcohol containing hydrochloric acid dissolves it with effervescence. It has a strong burning taste.

		Calculation.		Experiment.	
13 C	. . .	78	24·00	23·93	23·40
15 H	. . .	15	4·62	4·74	5·00
2 Pb	. . .	208	64·00	63·87	63·74
3 O	. . .	24	7·38	7·46	7·86
$C_{12} H_{15} Pb_2 O, CO_2$		325	100·00	100·00	100·00

Sulphate.—When sulphuric acid is added by drops to an alcoholic solution of the oxide, leaving the base in excess, a dazzling white crystalline precipitate of the sulphate is obtained, which must be washed with alcohol, and afterwards with ether. The salt is nearly insoluble in water, absolute alcohol, and ether, but dissolves readily in alcohol mixed with sulphuric or hydrochloric acid. From the acid solution it crystallises in tolerably large, hard, shining octohedral crystals.

				Löwig.			
12 C	. .	72	20·90	20·30	20·33	—	—	—
15 H	. .	15	4·30	4·48	4·60	—	—	—
2 Pb	. .	208	60·60	61·40	60·30	59·5	60·6	60·4
O	. .	8	2·54	2·08	3·10	—	—	—
SO_3	. .	40	11·66	11·74	11·67	—	—	—
$C_{12} H_{15} Pb_2 O, SO_3$		343	100·00	100·00	100·00			

Iodide, $(C_4H_5)_3Pb_2I_2$.—Formed by the action of iodide of potassium on sulphate of methyloplumbethyl. Very insoluble. When an alcoholic solution of iodide of potassium is added to a solution of the sulphate acidulated with sulphuric acid, the mixture shaken up with ether, the ethereal solution of iodide of methyloplumbethyl separated by water and abandoned to spontaneous evaporation, iodide of lead separates from it in considerable quantity. By rapid evaporation, a colourless oily residue is obtained, having a penetrating odour, and likewise yielding a deposit of iodide of lead. If the compound, while yet undecomposed, be distilled with water, the separation of iodide of lead takes place immediately, and the watery vapour which passes over is accompanied by a colourless, mobile, very pungent liquid, having an odour like that of oil of mustard, and no longer subject to spontaneous decomposition. This liquid was found to contain: 15·11 per cent. C, 5·70 H, 36·58 Pb, and 34·16 I,—numbers agreeing pretty nearly with the formula $(C_4H_5)_{12}Pb_4I_3$ [or $(Ae_3Pb)_4I_3$], which requires 25·02 C, 5·24 H, 36·40 Pb, and 33·34 I.

Bromide.—Obtained by adding an alcoholic solution of bromide of potassium to a solution of the sulphate in alcohol containing sulphuric acid; agitating the whole with ether, then with water to separate the ethereal solution; and evaporating the latter. The bromide then crystallises in long needles.

	Calculation.		Experiment.	
12 C . . .	72	19·20	—	—
15 H . . .	15	4·00	—	—
2 Pb . . .	208	55·47	—	—
Br . . .	80	21·33	20·96	21·23
$C_{12}H_{15}Pb_2Br$. .	375	100·00		

Chloride.—Obtained by adding chloride of barium to a solution of the sulphate in alcohol containing hydrochloric acid, agitating with ether, separating the ethereal solution by water, and leaving it to evaporate. Crystallises in beautiful long needles, having a strong lustre, and giving off a strong odour of oil of mustard when gently heated. When heated in a glass tube, they detonate slightly even at a moderate heat, yielding chloride of lead and metallic lead.

	Calculation.		Experiment.	
12 C . . .	72·0	21·79	21·58	21·51
15 H . . .	15·0	4·54	4·85	4·71
2 Pb . .	208·0	62·92	62·66	62·74
Cl . .	35·4	10·71	10·54	10·58
$C_{12}H_{15}Pb_2Cl$ . .	330·4	100·00	99·63	99·54

Nitrate.—Obtained by decomposing the alcoholic solution of the plumbethyls (page 268) with nitrate of silver. On evaporating the

alcoholic solution, the salt remains in the form of a colourless viscid liquid, which smells like butter, has a burning taste, and solidifies after a while in a crystalline unctuous mass. Decomposes by heat, with slight detonation. Dissolves readily in alcohol and in ether: the alcoholic solution, when slowly evaporated, deposits a small quantity of nitrate of lead.

Researches in Organic Chemistry.*

By Adolph Strecker.

1. *On the Composition of Tannic Acid.*

Tannic acid, and the tannins in general, are much more complex substances than is commonly supposed. Under the influence of mineral acids, alkalies, or ferments, they take up the elements of water, and are converted into glucose [grape-sugar] and a new acid. This decomposition, announced by the author two years ago, has served as a point of departure for determining the formula of tannic acid.

According to the analyses made by Pelouze, Liebig, and Berzelius, the molecule of tannic acid is expressed by the formula $C_{18}H_8O_{12}$; and it is supposed that in the neutral tannates 3 at. of the water contained in the acid are replaced by 3 at. of a metallic oxide. There is, however, but one tannate known, viz. the tannate of lead, which, according to analysis, contains carbon and metal in the ratio of 18 at. to 3 at.

The decomposition of tannic acid into glucose, $C_{12}H_{12}O_{12}$, and gallic acid, $C_{14}H_6O_{11}$, having shown that the above formula cannot represent the molecule of the acid, the following experiments were undertaken to determine the real formula:—

Tannic acid, prepared by Pelouze's method, was purified in two ways: first, by dissolving in pure ether and precipitating by water; secondly, by dissolving in water and precipitating by ether. Under these circumstances, two or three distinct strata of liquid are obtained, the heaviest of which is tannic acid absorbed by ether. This syrupy liquid was dissolved in water, evaporated *in vacuo*, and the residue analysed after drying at 120°. Ten analyses, made with oxide of copper in a current of oxygen, and with the products of seven different preparations, yielded results agreeing with the formula $C_{54}H_{22}O_{34}$.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	Calculation.	
C	52·1	52·2	52·2	52·2	52·2	52·3	52·1	52·2	52·3	52·3	C_{54}	52·4
H	3·8	3·8	3·7	3·7	3·6	3·9	3·8	3·6	3·7	3·5	H_{22}	3·6
O	—	—	—	—	—	—	—	—	—	—	O_{34}	44·0
												100·0

* Compt. rend. xxxix. 49.

According to this formula, the resolution of tannic acid into gallic acid and glucose is represented by the equation

$$C_{54}H_{22}O_{34}+8\,HO=3\,C_{14}H_6O_{10}+C_{12}H_{10}O_{10}.$$

This equation is confirmed by the quantities of gallic acid and glucose resulting from the decomposition. For the former, Mr. Wetherill found 87 per cent. as a maximum; for the glucose, the author obtained 22 per cent.

The quantity of water in the molecule $C_{54}H_{22}O_{34}$ which may be replaced by a metallic oxide, was determined directly by digesting tannic acid with oxide of lead, and also by the analysis of the neutral and basic salts. By the former method it was found that the acid loses 4 per cent. or 3 at. of water,—a result which is confirmed by the analysis of the lead-salts obtained by precipitation, in which the composition of the anhydrous acid is represented by the formula $C_{54}H_{19}O_{31}$, differing by 3 at. water from the formula $C_{54}H_{22}O_{34}$. The precipitates obtained with tannic acid and acetate of lead contain, for 54 at. C, from 3 to 10 at. oxide of lead.

The analyses of the tannates made by Pelouze, Liebig, Berzelius, Mulder, and Buchner, agree with the new formula of tannic acid, if we suppose that some of these salts do not give up all their water at 100°, or that they were not completely dried.

Tannic acid combines, according to Berzelius, with sulphuric and hydrochloric acids, when these acids are added to a solution of tannic acid in water, forming precipitates which redissolve it first, and become permanent only when the liquid contains an excess of sulphuric or hydrochloric acid. These compounds differ from conjugated acids in this respect, that the mineral acid cannot be separated from them by baryta- or silver-salts. The analysis of these precipitates shows that they are nothing but tannic acid impregnated with the acid liquid from which they have been deposited. In fact, the sulphuric tannin contains only from 2 to 4 per cent. of sulphuric acid, and the hydrochloric compound gives up all its hydrochloric acid when placed over quicklime *in vacuo*. Moreover, these precipitates exactly resemble tannic acid acidulated with a small quantity of mineral acid. The formation of a precipitate by mineral acids in a solution of tannin is therefore an effect of the same nature as its precipitation from the same solution by common salt or other alkaline salts, or even by ether, and is due simply to a diminution of the solubility of the tannin produced by changing the solvent.

Gallic acid, which, according to some chemists, contains in the formula $C_{11}H_6O_{10}$ either 4 or 2 equivalents of water, is, according to Strecker's analyses, a tribasic acid; and the yellow lead-salt, which Liebig and Buchner regard as a neutral salt, and represent by the formula $4\,PbO,\,C_{14}H_2O_6$, is a basic salt, which, when dried at 120°, has a composition represented by the formula

$$4\,PbO,\,C_{14}H_3O_7,\text{ or }3\,PbO,\,C_{14}H_3O_7+PbO.$$

In fact, five analyses made with the products of different preparations gave 75·9 to 76·1 per cent. PbO,—numbers approaching much more nearly to those required by the latter formula than to that of Liebig and Pelouze.

2. *On the Decomposition of Brucine by Nitric Acid.*

The remarkable reaction of brucine with nitric acid, in which the two colourless bodies, as soon as they come in contact, assume a red colour and give off gas, has never been explained, notwithstanding the experiments of Gerhardt, Liebig, Laurent, and Rosengarten.

Gerhardt found that the gas evolved in this reaction, which he did not succeed in condensing, had the odour and some other properties of nitrous ether ($C_4 H_5 O, NO_5$); so that he entertained no doubt as to its being really that compound. Liebig, perhaps by using dilute nitric acid, obtained a liquid heavier than water, and boiling at 70°,—totally different, therefore, from nitrous ether. Laurent, in repeating Gerhardt's experiments, condensed, in a bulb surrounded with a freezing mixture, a liquid, which he rectified, without seeing it boil, at a temperature not exceeding +10°, and which yielded by analysis 29·0 per cent. carbon and 6·1 per cent. hydrogen. These numbers do not agree very well with the composition of nitrous ether, which contains 32·0 per cent. carbon and 6·6 hydrogen; nevertheless, Laurent thought he had obtained sufficient evidence of the liquid being really nitrous ether. Laurent likewise analysed the yellow body which remained in the retort after the completion of the action. This body he named *Cacotheline*, and from two analyses not agreeing very well with each other, he assigned to it the formula $C_{42} H_{22} N_4 O_{20}$. For the decomposition of brucine by nitric acid he gives the equation

$$C_{48} H_{26} N_2 O_8 + 3\,NO_6 H = C_{42} H_{22} N_4 O_{20} + C_4 H_5 O, NO_3 + 2\,HO.$$

Rosengarten, who endeavoured to verify this formula by quantitative determinations, found that the volatile and inflammable body which is given off contains carbon and hydrogen nearly in the ratio of 4 at. to 6 at.; so that it could not be pure nitrous ether. Moreover, the analyses which he made of the yellow body yielded numbers which did not agree exactly with Laurent's formula. Not being able either to condense the volatile product or determine the equivalent of cacotheline by the analysis of its compounds, the only conclusion which Rosengarten deduced from his experiments was, that Laurent's formula does not represent correctly the decomposition of brucine by nitric acid.

The determination of the question whether nitrous ether is really formed in this reaction, presented peculiar interest, as no previous instance had been observed of the formation of an ethyl-compound, otherwise than from sugar or alcohol. As to ethylamine, which is

said to have been obtained from various alkaloids, there is nothing to show that the body actually obtained was not the isomeric base, dimethylamine.

The author therefore repeated the experiments of Laurent and Gerhardt with 28 grms. of melted brucine; the gas which was evolved was made to pass, first through a solution of potash of sp. gr. 1·2, then through a solution of protosulphate of iron, then over chloride of calcium, and lastly into a vessel cooled to −40°. A liquid soon condensed in this vessel, green at first, but soon changing to yellow. Bubbles of gas passed through this liquid during the whole course of the action, assuming an orange-red colour as soon as they mixed with the air.

The liquid thus condensed (3 or 4 grms.) was very volatile, boiled at −12·°5, had an odour resembling that of nitrous ether, and burned with a pale flame, slightly tinged with green. It gave by analysis numbers in the ratio of 2 at. carbon to 3 at. hydrogen and 1 at. nitrogen, and when treated with an alcoholic solution of potash yielded crystals of nitrite of potash. Hence it is the *nitrite of methyl*, C_2H_3O, NO_3. The author likewise prepared this new compound with wood-spirit, nitric acid, and arsenious acid, and found it to have the same properties and composition as the volatile liquid obtained from brucine.

The action of nitric acid upon brucine is so definite, that it enables us to determine the quantity of nitrite of methyl evolved from 1 at. of brucine. For this purpose an apparatus was used similar to the former, excepting that the product, instead of being condensed, was burned with oxide of copper. In this manner 1 at. brucine (394 pts.) yielded 2·1 at. carbonic acid and 2·98 at. water, corresponding to 1 at. nitrite of methyl.

These results agree with those of Gerhardt and Rosengarten, although these chemists did not ascertain correctly the nature of the volatile product; but it is difficult to explain the results obtained by Laurent. The product obtained by Liebig was probably nitrate of methyl, C_2H_3O, NO_5, which, according to Dumas and Peligot, boils at 66°, and is heavier than water. The nitrous acid in the warm dilute liquid was probably resolved into nitric acid and nitric oxide, the former of which united with the oxide of methyl.

With regard to the non-volatile products of the action, also, Strecker's results differ considerably from those obtained by Laurent. The yellow body, cacotheline, precipitated on diluting the acid liquid in the retort with water, is not the only fixed product, a large quantity of oxalic acid being in fact obtained at the same time. Among the volatile products, also, a considerable quantity of nitrous oxide and carbonic acid is evolved: the latter, however, is merely a secondary product, derived from the oxalic acid.

The formula of cacotheline is $C_{40}H_{22}N_4O_{18}$.

	Calculation.		Experiment (mean).
40 C . . .	240	51·9	52·1
22 H . . .	22	4·8	4·9
4 N . . .	56	12·1	12·6
18 O . . .	144	31·2	30·4
$C_{40}H_{22}N_4O_{18}$.	462	100·0	100·0

This formula was confirmed in two ways: First, by determining the quantity of oxalic and carbonic acid formed during the action of nitric acid upon brucine: of the 46 at. of carbon contained in brucine, 4 at. are separated in the form of oxalic and carbonic acid; and deducting from 46 C the 2 C of the methyl and these 4 C, we find that cacotheline must contain 40 C. Secondly, by the analysis of its definite compounds. Cacotheline is, in fact, a nitrous base; but its compounds with acids are decomposed by water. When a solution of chloride of platinum is poured into a solution of cacotheline in hydrochloric acid, there is formed after some hours a crystalline precipitate containing 14·8 per cent. of platinum. This agrees with the formula

$$C_{40}H_{22}N_4O_{18} . HCl . Pt\,HCl_2.$$

Cacotheline combines also with metallic oxides; with baryta it forms a soluble compound containing

$$C_{40}H_{22}N_4O_{18} . Ba\,O.$$

According to these experiments, the equation which represents the decomposition of brucine by nitric acid is

$$\underbrace{C_{46}H_{26}N_2O_8}_{\text{Brucine.}} + 5\,(HO . NO_5) =$$

$$\underbrace{C_{40}H_{22}N_4O_{18}}_{\text{Cacotheline.}} + \underbrace{C_2H_3O . NO_3}_{\text{Nitrite of Ethyl.}} + \underbrace{C_4H_2O_8}_{\text{Oxalic Acid.}} + 2\,NO_2 + 4\,HO.$$

Brucine therefore contains carbon in three different groups: one of these is methyl; the others are transformed by nitric acid into cacotheline and oxalic acid. Cacotheline is doubtless a nitro-compound containing 2 at. of hyponitric acid, and may therefore be regarded as a derivative of the normal base $C_{40}H_{24}N_2O_{10}$, differing from quinine by only 6 at. oxygen.

3. *On Hydrocyanaldine.*

Strecker showed some years ago, that a mixture of aldehydate of ammonia and hydrocyanic acid evaporated over the water-bath, together with an excess of hydrochloric acid, yields a residue of hydrochlorate of ammonia and alanine.

$$C_4H_4O_2 . NH_3 + 2\,HCl + C_2NH + 2HO = \underbrace{C_6H_7NO_4 . HCl}_{\text{Hydrochlorate of Alanine.}} + NH_4Cl.$$

A totally different action takes place when the mixture is not heated. In this latter case, there are formed in the liquid, after a few days, a number of colourless crystals, which gradually increase. To this body the author gives the name *Hydrocyanaldine*. It is insipid; has no action on vegetable colours; dissolves in water and in ether, but more readily in alcohol. It melts at a slightly elevated temperature, and sublimes at a moderate heat. When suddenly heated it decomposes, giving off an odour like that of hydrocyanic acid. The solution of this body is not precipitated by silver-salts, not even after the addition of nitric acid; but on subsequently heating the liquid, aldehyde is evolved and cyanide of silver precipitated. Heated with potash, it gives off ammonia, the solution acquiring a brown colour, and aldehyde-resin separating from it.

The analysis of hydrocyanaldine leads to the formula

$$C_9 H_6 N_2, \text{ or } C_{18} H_{12} N_4,$$

and its formation is expressed by the equation

$$3(\underbrace{C_4H_4O_2.NH_3}_{\text{Aldehydate of Ammonia.}}) + 3\,C_2HN + 2\,HCl = C_{18}H_{12}N_4 + 2\,NH_4Cl + 6\,HO.$$

This reaction exhibits some analogy with the formation of thialdine:

$$3\,(C_4\,H_4\,O_2\,.\,NH_3) + 6\,HS = \underbrace{C_{12}\,H_{13}\,NS_4}_{\text{Thialdine.}} + 2\,NH_4\,S + 6\,HO.$$

Hydrocyanaldine differs, however, considerably from thialdine,—chiefly in not exhibiting decided basic properties.

4. *On a New Mode of Formation of Propionic Acid.*

If, according to Bensch's process, a mixture of cane-sugar (boiled with a small quantity of tartaric acid), chalk, and old cheese, be left to itself in a warm place at the temperature of 30°, the mass is converted, in the course of eight or ten days, into a thick magma of lactate of lime. The mother-liquors contain a small quantity of mannite, which is difficult to extract. But, according to Strecker's experiments, this mixture behaves in a totally different manner at low temperatures, the fermentation then going on very slowly, and a very large quantity of mannite being formed. A mixture of this kind, prepared according to Bensch's directions, with 5 kilogrammes of sugar, having been left during winter in a room which was heated during the day only, it was only after the lapse of two or three months that crusts of lactate of lime were deposited; the mother-liquor, concentrated by evaporation, yielded fresh quantities of lactate of lime, together with a multitude of mannite crystals, which were easily purified by several crystallisations. The quantity of lactate of lime did not appear to exceed that of the mannite. We know, from

the experiments of Pelouze and Gay-Lussac, that the juice of beet-root likewise yields a considerable quantity of mannite by viscous fermentation; but the conditions of its fermentation are different.

A mixture which had deposited crusts of lactate of lime was left during summer in a place the temperature of which did not exceed 20° or 22°, the water being renewed as it evaporated. After some months, the volatile acids which had formed were separated. There was not a trace of butyric acid, but there were very large quantities of propionic and acetic acids. The two acids were separated by Liebig's method, viz. partial saturation with potash, and distillation. The propionic acid passed over first, and the residue contained the acetic acid.

With this propionic acid the following salts were prepared and analysed:—

$KO, C_6 H_5 O_3,$	thin laminæ.
$NaO, C_6 H_5 O_3 + 2\,HO,$	amorphous mass, dried in the air.
$BaO, C_6 H_5 O_3 + HO,$	crystals of the rhombic system, soluble in 1·3 part water at 15°.
$CaO, C_6 H_5 O_3 + HO,$	silky pallets.
$CuO, C_6 H_5 O_3 + HO,$	green crystals, probably isomorphous with the acetate.
$2\,PbO, C_6 H_5 O_3,$	needles.

5. *On some Compounds of Hydrargomethyl and Hydrargethyl.*

Frankland found, a short time ago, that iodide of methyl and iodide of amyl, exposed to the sun's rays in contact with mercury, form crystals whose composition is represented by the formulæ $C_2 H_3 Hg_2 I$, and $C_{10} H_{11} Hg_2 I$: to these bodies he gives the names, iodide of hydrargomethyl and iodide of hydrargamyl. Frankland did not succeed in producing a similar compound with iodide of ethyl, although its existence may be reasonably presumed.

Strecker, however, before he was acquainted with Frankland's experiments, had already obtained the iodide of hydrargethyl, which, indeed, is easily produced from a mixture of iodide of ethyl and mercury at ordinary temperatures, under the influence of diffused daylight. Crystals are formed after a while, increasing in quantity till the liquid solidifies in a mass. The crystals dissolve in ether and in alcohol, and separate from the solutions in thin, colourless, very brilliant laminæ. They sublime at 100°, but do not melt till very strongly heated. They are insoluble in water, but dissolve in ammonia and in potash-ley, from which they may be recrystallised without decomposition. Their composition is represented by the formula $C_4 H_5 Hg_2 I$. The solution treated with nitrate of silver yields iodide of silver and nitrate of hydrargethyl, $C_4 H_5 Hg_2 O . NO_5$, which crystallises by evaporation in colourless prisms. Chloride of sodium added to the aqueous solution of this salt throws down the chloride of hydrargethyl, $C_4 H_5 Hg_2 Cl$, which closely resembles the iodide. All these ethyl-

compounds are decomposed by the direct rays of the sun, and that is why Frankland did not succeed in preparing them.

Strecker has also prepared the nitrate of hydrargomethyl, and finds its composition to be $C_2 H_3 Hg_2 O, NO_5 + HO$.

6. *On the Constitution of Quinine.*

Notwithstanding the great importance of quinine, chemists are much less acquainted with it than with a host of other bodies which present no interest whatever in a practical point of view; they are not, in fact, agreed about either its ultimate constitution, its equivalent, or its atomic weight,—questions which must all be determined before we can enter upon the problem of *composing* quinine.

The ultimate constitution of quinine is at present expressed by the formula

$C_{19} H_{11} NO_2$ (Laurent), or
$C_{20} H_{12} NO_2$ (Liebig).

This question is easily resolved by the analysis of pure quinine. Strecker prepared the base from commercial sulphate of quinine, obtained from M. Merck in a very pure state, and further purified by repeated crystallisation. The analysis of quinine dried at 120°, which was performed with oxide of copper and oxygen gas, yielded the ratio $C_{20} H_{12} NO_2$; or, in 100 parts—

	Calculated.	Found.	
Carbon	74·1	74·0	74·1
Hydrogen	7·4	7·5	7·5
Nitrogen	8·6	—	—
Oxygen	9·9	—	—
	100·0		

This formula was likewise confirmed by the analysis of several of the compounds.

Nitrate of Quinine.—Sulphate of quinine precipitated by nitrate of baryta yields by spontaneous evaporation colourless rhombic crystals. The analysis of this compound, purified by several crystallisations, leads to the formula $C_{40} H_{24} N_2 O_4 . HO . NO_5$; or, in 100 parts—

	Calculated.	Found.
Carbon	62·0	62·1
Hydrogen	6·5	6·6

The *Sulphate of Quinine*, from which the base was prepared, yielded, when dried at 120°, 10·7 and 10·8 per cent. of sulphuric acid,—numbers which agree almost exactly with the formula

$C_{40} H_{24} N_2 O_4 . HO . SO_3$ (calc. quantity of $SO_3 = 10·7$ per cent.)

An alcoholic solution of quinine forms with nitrate of silver a crystalline precipitate which dissolves in boiling water. The solution, when left to cool, solidifies in a mass having the aspect of starch;

but changing after a while to colourless prisms. These crystals consist of a compound of quinine and nitrate of silver; they require 300 parts of cold water to dissolve them. Analysis leads to the formula

$$C_{40}H_{24}N_2O_4 . AgO . NO_5.$$

With regard to the equivalent of quinine, some chemists represent it by the formula $C_{20}H_{12}NO_2$; others are of opinion that it should be $C_{40}H_{24}N_2O_4$. According to the first formula, neutral sulphate of quinine is $C_{20}H_{12}NO_2 . HO . SO_3$; and the other sulphate, $C_{40}H_{24}N_2O_4 . HO . SO_3$, must be regarded as a basic salt. But, according to the other formula, the latter is the neutral salt, while the sulphate, $C_{20}H_{12}NO_2 . HO . SO_3$, is an acid salt, whose true formula is $C_{40}H_{24}N_2O_4 . 2\,HO . 2\,SO_3$.

Lastly, there are some chemists who represent the equivalent of quinine by $C_{20}H_{12}NO_2$, but regard the molecule as composed of two equivalents, or as $C_{40}H_{24}N_2O_4$.

The facts hitherto known afford no very decided reasons for adopting either of these formulæ in preference to the other, but the following results may perhaps serve to decide the question:—

A mixture of iodide of ethyl and quinine dissolved in ether yields, after some hours, a quantity of crystals, which continually increase. These crystals dissolve readily in boiling water, and separate from it in long needles ranged around a common centre. They are colourless, silky, and have a bitter taste; they give off no water at 100°, but melt without decomposition at a higher temperature.

The composition of these crystals is expressed by the formula $C_{44}H_{29}N_2O_4I$; or, in 100 parts—

	Calculated.	Found.	
Carbon . . .	55·0	55·0	54·8
Hydrogen . .	6·0	6·2	6·2
Iodine . . .	26·5	26·4	

The formation of this compound, which may be called *Ethyloquinine*, is represented by the equation

$$C_{40}H_{24}N_2O_4 + C_4H_5I = C_{44}H_{29}N_2O_4I.$$

A similar compound is obtained with iodide of methyl. The composition of *iodide of methyloquinine* is expressed by the formula $C_{42}H_{27}N_2O_4I$; or, in 100 parts—

	Calculated.	Found.
Carbon . .	54·1	54·2
Hydrogen .	5·8	5·9
Iodine . .	27·2	26·9

The solution of these iodides in water is not precipitated by ammonia, and potash produces a cloud in the solution only when added in great excess. The precipitate thus obtained dissolves in boiling water, and the solution yields crystals identical with the former: in fact, the iodide is not decomposed by the potash, but is insoluble in potash-

ley. With oxide of silver the solution of the iodides yields iodide of silver, and the solution retains a very energetic base, which rapidly absorbs carbonic acid from the air, forming crystals which have an alkaline reaction. Ethyloquinine is obtained, by evaporating the solution *in vacuo*, as an amorphous mass, which dissolves in alcohol, and is precipitated therefrom by ether in colourless crystals. It decomposes at 120°. The following salts of this base have been prepared:—

Neutral Sulphate of Ethyloquinine	$C_{44}H_{29}N_2O_5 . SO_3$
Acid Sulphate	$C_{44}H_{29}N_2O_5 . SO_3 + HO$
Chloride	$C_{44}H_{29}N_2O_4 . Cl$
Platinum-salt	$C_{44}H_{29}N_2O_4 . Cl, HCl . 2PtCl_2$

All the properties of these compounds show that ethyloquinine belongs to the fourth class of Hofmann's bases; it is a base corresponding to oxide of ammonium, NH_4O. Quinine is therefore a nitrile base (of the third class), and contains, in the molecule $C_{40}H_{24}N_2O_4$, three compound radicals. It can, therefore, no longer be doubted that the molecule and equivalent of quinine should be expressed by the formula $C_{40}H_{24}N_2O_4$. As to the compound radicals which compose it, the facts at present known do not enable us to decide upon their nature.

7. *On the Artificial Production of Oil of Cinnamon.*

The author showed some years ago that styrone, the substance obtained by treating styracine with potash, in the state of concentrated or alcoholic solution, is the *alcohol* of cinnamic acid; inasmuch as it bears to that acid the same relation that common alcohol bears to acetic acid. Experiments made by M. Wolff, at the author's suggestion, further showed that styrone may, by the action of powerful oxidising agents, be converted into cinnamic acid.

The following experiments show that styrone, when subjected to the same conditions as those under which alcohol is transformed into aldehyde, yields cinnamic aldehyde or oil of cinnamon.

When platinum-black is moistened with liquid styrone, and the mixture exposed to the air for some days, the greater part of the styrone is transformed into cinnamic aldehyde, which may be separated from the unaltered styrone by the excellent process of M. Bertagnini. With a strong solution of bisulphite of potash, crystals are obtained which must be washed with ether to free them from styrone. The crystals, when treated with dilute sulphuric acid, yield cinnamic aldehyde in the pure state. The same crystals dissolve in nitric acid, and the solution, after a few seconds, yields crystals of nitrate of cinnamic aldehyde.

The transformation of styrone into cinnamic aldehyde by atmospheric oxidation, takes place as represented by the equation

$$\underbrace{C_{18}H_{10}O_2}_{\text{Styrone.}} + 2\,O = \underbrace{C_{18}H_8O_2}_{\text{Cinnamic Aldehyde.}} + 2\,HO$$

8. *On the Artificial Production of Taurin.*

The properties of taurin lead to the idea that it may be produced artificially. Redtenbacher endeavoured to form it from aldehyde and bisulphite of ammonia, but he merely obtained an isomeric compound possessing different properties.

The following experiments were tried by Strecker, to attain the same object :—

Sulphate of methyl, $C_2 H_3 O, SO_3$, treated with ammonia, yields sulphomethylane and wood-spirit, according to the equation

$$2 (C_2 H_3 O . SO_3) + NH_3 = C_2 H_5 NS_2 O_6 + C_2 H_4 O_2.$$

With sulphate of ethyl, therefore, one might expect to obtain taurin, provided the reaction were similar:

$$2 (C_4 H_5 O . SO_3) + NH_3 = C_4 H_7 NS_2 O_6 + C_4 H_6 O_2.$$

In reality, however, sulphate of ethyl behaves in a different manner, yielding a conjugated acid, sulphethamic acid, described by the author some years ago.

Sulphate of methyl treated with methylamine instead of ammonia might, according to analogy, yield taurin:

$$2 (C_2 H_3 O . SO_3) + C_2 H_5 N = C_4 H_7 NS_2 O_6 + C_2 H_4 O_2.$$

This mode of formation was not tried, as experiment had previously shown that taurin, when decomposed by potash, does not yield a trace of methylamine.

Nitrite of ethyl, $C_4 H_5 O . NO_3$, which Gerhardt places among nitro-compounds, $\left.\begin{matrix} C_4 H_5 \\ NO_4 \end{matrix}\right\}$, would, if it acted like nitronaphthalin, yield taurin (or the isomeric body) when treated with bisulphite of ammonia.

Nitronaphthalin and bisulphite of ammonia yield, according to Piria, naphthionic acid and sulphate of ammonia:

$$\underbrace{C_{20} H_7 NO_4}_{\text{Nitronaphthalin.}} + 6 SO_2 + 2 HO = \underbrace{C_{20} H_9 NS_2 O_6}_{\text{Naphthionic Acid.}} + 4 SO_3$$

By analogy, therefore, we might have with nitrous ether—

$$\underbrace{C_4 H_5 NO_4}_{\text{Nitrous Ether.}} + 6 SO_2 + 2 HO = \underbrace{C_4 H_7 NS_2 O_6}_{\text{Taurin.}} + 4 SO_3.$$

But experiment shows that nitrite of ethyl, when treated with bisulphite of ammonia, does not behave like nitronaphthalin, but gives off ammonia and yields sulphuric and sulphovinic acids.

Isethionic acid, which, according to Regnault, is prepared from anhydrous sulphuric acid and olefiant gas, forms with ammonia a salt which differs in composition from taurin only by two atoms of water:

$$NH_4 O . C_4 H_5 O . 2 SO_3 = C_4 H_7 NS_2 O_6 + 2 HO.$$

This salt melts at 120° without evolving ammonia, but when heated to 200° begins to diminish in weight from loss of water. It was

heated to 230°, and maintained at that temperature till it had lost 11 per cent. of its weight. The mass was then dissolved in water, forming a solution which yielded a crystalline precipitate on addition of alcohol; and on dissolving this precipitate in water, and evaporating, large crystals were obtained, exactly resembling those of taurin from bile. They sustain, like taurin, a temperature of 240° without melting or becoming coloured; do not give off ammonia when treated with potash-ley, or precipitate baryta-salts after being boiled with nitric acid or aqua-regia. Fused with potash or nitre, they give off ammonia, and the mass contains sulphuric acid. All these properties being the same as those of taurin, and the mode of formation showing that the composition of the crystals must agree with that of taurin, it follows that this product is identical with taurin obtained from bile.

On the Compounds of Glycerine with Acids.*

By M. Berthelot.

A considerable number of these compounds were described in a former paper.† The results detailed in the present memoir relate—

1. To the study of various glyceric compounds of the highest order;
2. To various hydrochloric compounds of glycerine;
3. To the action of this body on oxalic acid;
4. To a peculiar compound of glycerine and alcohol.

The description of these products is followed by some general considerations on the constitution of glycerine-compounds.

I.—The following compounds have been prepared:—

1. *Triolein*, $C_{114}H_{104}O_{12}=3\,C_{36}H_{34}O_4+C_6H_8O_6-6\,HO$. This body is liquid and neutral. Treated with oxide of lead at 100°, it is resolved slowly and with difficulty into oleic acid and glycerine. It is identical with natural olein, and exhibits the composition and properties of the olein analysed by Chevreul.

2. *Trivalerin*, $C_{36}H_{32}O_{12}=3\,C_{10}H_{10}O_4+C_6H_8O_6-6\,HO$. Neutral oily liquid, having an unpleasant odour, insoluble in water, soluble in alcohol and in ether; resolvable into glycerine and valerianic acid.

3. *Tributyrin*, $C_{30}H_{26}O_{12}=3\,C_8H_8O_4+C_6H_8O_6-6\,HO$. Neutral, oily, odoriferous liquid, having a density of 1·056, resolvable into glycerine and butyric acid.

4. *Tribenzoicin*, $C_{48}H_{20}O_{12}=3\,C_{14}H_6O_4+C_6H_8O_6-6\,HO$. This body is neutral. When purified, it crystallises in beautiful white needles, larger than those of any other compound of the glyceric series.

5. *Triacetin*, $C_{18}H_{14}O_{12}=3\,C_4H_4O_4+C_6H_8O_6-6\,HO$. Neutral odoriferous liquid, of density equal to 1·174, insoluble in water, but

* Compt. rend. xxxviii. 668.

† Ibid. xxxvii. 398; Chem. Soc. Qu. J. vi. 280.

very soluble in dilute alcohol. Contains C=49·9; H=6·8. The formula requires C=49·6; H=6·4.

Triacetin is resolved by saponification into acetic acid and glycerine. When thus decomposed it yields—

Acetic acid	80·6
Glycerine	43·1
	123·7

The formula requires—

Acetic acid	82·6
Glycerine	42·2
	124·8

From the analytical results obtained by the examination of these bodies, and especially by the analysis and saponification of triacetin, the one which has the lowest equivalent, the author has been led to modify the usually-received formula of natural stearin,* which in his previous memoir he had thought himself justified in retaining.

According to these results, and admitting that the glyceric compounds of the highest order have all similar formulæ, natural stearin, as well as the artificial compound which is identical with it, must be regarded as a *tristearin*.

$$C_{114}H_{110}O_{12}=3\,C_{36}H_{36}O_4+C_6H_8O_6-6\,HO.$$

This formula agrees with the analyses and facts already ascertained. The same observation applies, with the same reservations, to natural margarin and palmitin. These bodies, as well as the artificial compounds identical with them, appear indeed to be *trimargarin* and *tripalmitin*.

II.—1. Besides the bodies above mentioned, M. Berthelot has prepared a new neutral compound of hydrochloric acid and glycerine.

Dichlorhydrin, $C_6H_6Cl_2O_2=2\,HCl+C_6H_8O_6-4\,HO$. Neutral limpid liquid, insoluble in water, and having a very decided ethereal odour. Sp. gr.=1·37. Potash decomposes it slowly, with reproduction of glycerine and hydrochloric acid.†

2. The author has specially examined the compounds formed by glycerine and acids, with the assistance of hydrochloric acid. According to their analysis, their properties, and the comparatively low temperature at which they distil, these bodies appear to be formed, not by the union of primary compounds, but by definite complex substances, into which hydrochloric acid enters together with the other acid neutralised by the glycerine. According to this supposition, a glyceric compound may contain several different acids, as

* This is the formula given by Lecanu and Berzelius, calculated with the equivalent of stearic acid now adopted. The formula of Pelouze and Liebig differs from it by only 2 equivs. of water.

† The existence and nature of this compound have led to new researches on acetidin and butyridin. According to new experiments and saponifications, acetidin is a *diacetin*, $C_{14}H_{12}O_{10}=2\,C_4H_4O_4+C_6H_8O_6-4\,HO$, and butyridin a *dibutyrin*.

well as several equivalents of the same acid. One of these compounds, *Benzochlorhydrin*, appears by analysis to have the definite formula

$$C_{20}H_{11}ClO_6 = C_{14}H_6O_4 + HCl + C_6H_8O_6 - 4\,HO.$$

III.—Oxalic acid heated to 100° in contact with glycerine is resolved into pure carbonic acid, which escapes, and formic acid, which remains with the glycerine,—without, however, forming a neutral compound. If the glycerine is in excess, the decomposition is complete at the end of twenty-seven hours. This curious reaction is in accordance with the frequently-observed production of formic acid at the expense of oxalic acid; but this phenomenon has perhaps never before exhibited so completely the pure and simple character of a decomposition:

$$C_4H_2O_8 = C_2O_4 + C_2H_2O_4.$$

IV.—Glycerine forms with alcohol a compound analogous to the conjugated ethers discovered by Williamson.

Diethylin, $C_{14}H_{16}O_6 = 2\,C_4H_5Br + C_6H_8O_6 - 2\,HBr$, is prepared by mixing glycerine with hydrobromic ether and excess of potash, and heating the mixture to 100° for sixty hours in close vessels.* When the reaction is complete, the liquid in the tubes forms two layers. The upper layer is poured off and distilled. Diethylin distils over at 191°. It is a limpid, colourless oil, sufficiently mobile, scarcely if at all soluble in water, and has a faint ethereal and somewhat peppery odour. Its density is equal to 0·92. When a few drops of diethylin are thrown upon ignited lime, acrolein appears to be formed. Diethylin distilled with a mixture of sulphuric and butyric acids yields butyric ether.

General Conclusions.—1. From the facts above mentioned, and those contained in the former paper, it appears that the glyceric compounds are neutral bodies formed by the union of acids and glycerine in equivalent proportions.

In this union, which is attended with elimination of the elements of water, the properties of the acid become latent. When these bodies are treated with potash, a neutral salt is reproduced, and an equivalent quantity of another body formed,—the same for all, viz. glycerine. At the same time, the elements of water are fixed, and the properties of the acid reappear. These same phenomena of decomposition show themselves under the most varied circumstances, and often under the slightest influences.

These conditions, phenomena, and products are exactly the same as those which accompany the decomposition of the natural fats, as shown, forty years ago, by Chevreul.

2. These facts show, as Chevreul remarked, a connection between fats and ethers. On the one hand, the ethers, like fats, are formed by the union, either direct or mediate, of an acid with alcohol, the union being attended with separation of the elements of water and

* The author has prepared vinomethylic ether by a similar process with potash.

disappearance of the properties of the acid. On the other hand, the neutral compounds thus formed reproduce by the most various processes the acid and the alcohol, with fixation of the elements of water. By the action of alkalies, of concentrated acids, or of water, whether rapidly at 220°, or slowly at ordinary temperatures, the neutral fats are resolved into acids and glycerine, and the ethers in like manner into acids and alcohol.

With the one set of bodies, as with the others, the action of ammonia produces amides. But what is more, the equivalence of glycerine and alcohol in presence of acids may be demonstrated by direct and reciprocal actions; for we may at pleasure either decompose certain ethers with glycerine and produce a glyceric compound, or decompose a fat with alcohol and produce an ether.

These facts tend to show, independently of all hypothesis, the analogy of constitution existing between glyceric compounds and ethers.

3. If, however, glycerine resembles alcohol in the nature of the compounds which it forms with acids, still the formulæ of these same compounds, and the existence of several neutral compounds between glycerine and one and the same acid, establish a wide difference between glycerine and alcohol.

In fact, the neutral glyceric compounds may be arranged in three separate series:

The compounds of the first series, analogous to the ethers, even by their formulæ, are formed by the union of 1 equiv. of an acid and 1 equiv. of glycerine, with separation of 2 equivs. of water.

Monostearin . . . . . $C_{42} H_{42} O_3 = C_{36} H_{36} O_4 + C_6 H_8 O_6 - 2\,HO.$
Monochlorhydrin . . . . . $C_6 H_7 Cl O_4 = HCl + C_6 H_8 O_6 - 2\,HO.$

The second series is formed by the union of 2 equivs. of acid and 1 equiv. of glycerin, with separation of 2 or 4 equivs. of water:*—

Distearin . . . . . $C_{78} H_{78} O_{12} = 2\,C_{36} H_{36} O_4 + C_6 H_8 O_6 - 2\,HO.$
Dibutyrin . . . . . $C_{22} H_{22} O_{12} = 2\,C_8 H_8 O_4 + C_6 H_8 O_6 - 2\,HO.$
Diacetin . . . . . $C_{14} H_{12} O_{10} = 2\,C_4 H_4 O_4 + C_6 H_8 O_6 - 4\,HO.$
Benzochlorhydrin . . . . $C_{20} H_{11} Cl O_6 = C_{14} H_6 O_4 + HCl + C_6 H_8 O_6 - 4\,HO.$
Diethylin . . . . . $C_{14} H_6 O_6 = 2\,C_4 H_6 O_2 + C_6 H_8 O_6 - 4\,HO.$
Dichlorhydrin . . . . . $C_6 H_6 Cl_2 O_2 = 2\,HCl + C_6 H_8 O_6 - 4\,HO.$

The third series results from the union of 3 equivs. of acid and 1 equiv. of glycerine, with separation of 6 equivs. of water:

Tristearin . . $C_{114} H_{110} O_{12} = 3\,C_{36} H_{36} O_4 + C_6 H_8 O_6 - 6\,HO.$
Triolein . . . $C_{114} H_{104} O_{12} = 3\,C_{36} H_4 O_4 + C_6 H_8 O_6 - 6\,HO.$
Triacetin . . . $C_{18} H_{14} O_{12} = 3\,C_4 H_4 O_4 + C_6 H_8 O_6 - 6\,HO.$

It is to this last series that the natural fats belong. In the decomposition of bodies of this series, 3 KO unite with the anhydrous acid and replace the residue $C_6 H_5 O_3$, the oxygen in which is equal to one-third of that in the anhydrous acid, which ratio is the same as that in the neutral salts.

These facts show that glycerine bears to alcohol precisely the same relation that phosphoric acid bears to nitric acid. In fact, nitric acid

* The quantity of water eliminated is, perhaps, always the same.

forms but one series of neutral salts, whereas phosphoric acid produces three distinct series of salts, viz. the ordinary phosphates, pyrophosphates, and metaphosphates. These three series of salts, when decomposed by a strong acid in presence of water, reproduce one and the same phosphoric acid. In a similar manner, alcohol forms but one series of neutral ethers, whereas glycerine forms three distinct series of neutral compounds; and the bodies of all three series, when decomposed in presence of water, reproduce one and the same body, viz. glycerine.

Glycerine is not the only substance which shares with the alcohols the property of forming neutral and stable compounds by its union with acids in general. The same property is possessed in an almost equal degree by mannite. With this body and stearic acid the author has already formed *stearite;* with palmitic acid, *palmitite;* with butyric acid, *butyrite;* with acetic acid, *acetite;* and with hydrochloric acid, *chlorohydrite.* Several of these bodies, when decomposed by water at a high temperature, reproduce the acid from which they formed, and likewise crystallised mannite.

On Caprylic Alcohol and its Derivatives.*

By J. Bouis.

In a former paper†, the author made known the formation and properties of this new alcohol, reserving the complete description of it for a monograph which he was about to publish on Castor-oil. Peculiar circumstances having prevented the completion of this long work, the following extract from it is now published, relating to caprylic alcohol, in order to fix the composition of that body, which has been misconceived by some chemists who have repeated the author's experiments without being acquainted with all the details of the preparation.

Caprylic alcohol, $C_{16}H_{18}O_2$, is a transparent, colourless, oily liquid, which stains paper like essential oils; is insoluble in water, soluble in common alcohol, wood-spirit, ether, and acetic acid; and readily dissolves fats, resins, sulphur, phosphorus, and iodine. It burns with a very beautiful white flame; has no action upon polarised lights. Sp. gr. 0·823 at 17°. Boils without decomposition at 179°, under a a pressure of 0·760 m.

Sulphuric acid transforms this alcohol into sulphocaprylic acid, capable of uniting with bases, or else into a liquid hydrocarbon isomeric with ethylene, amylene, &c. This hydrocarbon is also produced from it by the action of fused chloride of zinc.

Caprylic alcohol is attacked by potassium and sodium, forming compounds in which part of the hydrogen is replaced by the metal.

* Compt. rend. xxxviii. 935.

† Ibid. xxxiii. 141; Chem. Soc. Qu. J. iv. 362.

Chloride of calcium combines with it, forming well-defined crystals; the compound is more soluble cold than hot; it is destroyed by water.

Castor-oil properly treated with potash always yields the fourth of its weight of sebacic acid, the fourth of its volume of perfectly colourless caprylic alcohol, and leaves a residue consisting of a mixture of fatty acids, one of which is liquid, and approaches in composition to oleic acid, the other solid, and has the composition of ethalic acid.

The alcohol, after being purified by several distillations over fragments of potash, distils completely without alteration of boiling point, and without even becoming coloured.

Numerous analyses of products obtained from American, French, and German castor-oil, agree exactly with the formula

$$C_{16}\,H_{18}\,O_2 = 4 \text{ vol.}$$

which has likewise been confirmed by several determinations of the vapour-density. Identical results were also obtained with the alcohol procured by treating ricinolic acid with potash.

The formula is further established by the composition of the following derivatives :—

Caprylene, $C_{16}\,H_{16}$, is a colourless, refracting liquid, having a somewhat powerful odour, insoluble in water, soluble in alcohol and ether, burning with a very bright flame. Sp. gr. = 0·0723 at 17°. Boils without decomposition at 125° under a pressure of 0·760 m. Vapour-density by calculation = 3·86 = 4 vol. The mean of several experiments gave 3·86.

This hydrocarbon was obtained by distilling the alcohol either with sulphuric acid or with fused chloride of zinc. The products obtained either with ordinary sulphuric acid, or with the Nordhausen acid, vary according to the duration of the action; being either sulphocaprylic acid, $2\,SO_3, C_{16}\,H_{17}\,O, HO$, or a mixture of caprylene and caprylic ether; or lastly, a hydrocarbon isomeric with caprylene, but possessing very different properties. This last-mentioned body has a density of 0·814, and boils towards 250°, the boiling point rapidly rising; its odour then becomes intolerable, resembling that of perspiration.

Sulphocaprylic acid is a colourless, syrupy liquid, very soluble in water and alcohol; blackens and decomposes when heated; its solution, when boiled, reproduces caprylic alcohol. It is obtained by exactly decomposing sulphocaprylate of baryta with dilute sulphuric acid, or the lead-salt with sulphuric acid, and evaporating the liquid in a dry vacuum.

Sulphocaprylate of baryta is white, of nacreous aspect, unctuous, very soluble in water and alcohol, from which it is sometimes deposited in needle-shaped crystals; it decomposes towards 100°, or when left too long in vacuo. After being pressed between folds of paper, it gave by analysis numbers agreeing exactly with the formula

$$2\,SO_3, C_{16}\,H_{17}\,O, Ba\,O + 3\,HO.$$

This salt is extremely bitter, but leaves a very sweet after-taste.

Sulphocaprylate of potash is white, nacreous, permanent in the air, very soluble in water and in alcohol. When heated it begins to melt, and burns with a bright flame, without charring. It is obtained from the baryta-salt by double decomposition, or by directly saturating the acid with carbonate of potash, with certain precautions mentioned in the author's memoir. It decomposes above 100°. Its composition is $2\,SO_3 . C_{16}\,H_{17}\,O . KO . HO$.

Calculation requires

$SO_3 . KO$	. . .	33·9
C	. . .	37·3
H	. . .	6·9

Experiment gave with two different products

$SO_3 . KO$	. . .	34·1	. 33·9
C	. . .	37·1	. 37·17
H	. . .	6·92	. 6·93

Acetate of Cayryl, $C_{16}\,H_{17}\,O . C_4\,H_3\,O_3$, is a liquid having a very agreeable odour, insoluble in water, boiling about 190° C. It may be readily obtained with caprylic alcohol, acetic acid, and a current of hydrochloric acid, or better with acetate of soda and sulphuric acid.

Chloride of Capryl, $C_{16}\,H_7\,Cl$, is liquid, insoluble in water, very slightly soluble in alcohol: the solution does not precipitate silver-salts. It burns with a smoky flame, green at the edges. Has a very decided odour of oranges. Its boiling point is nearly constant at 175°. It was prepared directly with hydrochloric acid and caprylic alcohol, or else with perchloride of phosphorus.

Iodide of Capryl, $C_{16}\,H_{17}\,I$, is very much like the preceding compound.

When chloride of capryl is acted upon by sodium, all the chlorine is removed, and the product of the action is *Capryl*, $\left.\begin{matrix}C_{16}\,H_{17}\\C_{16}\,H_{17}\end{matrix}\right\}$ or caprylene, $C_{16}\,H_{16}$, according as the process is performed at a high or a low temperature. In the cold, the sodium becomes covered with a pellicle of chloride, which, when detached by agitation, is replaced by a new one, till the chlorine is completely removed.

Analysis gives the following numbers for capryl:—

$$C = 85{\cdot}04 \quad H = 14{\cdot}99 \quad \left\{\begin{matrix}C_{16} & . & . & 84{\cdot}95\\H_{17} & . & . & 15{\cdot}04\end{matrix}\right.$$

If the action be assisted by heat, till the sodium appears to be no longer attacked, a liquid is obtained having the odour and density of caprylene, and, like that compound, boiling at 124°. Its formula is $C_{16}\,H_{16} = 4$ vol.

Analysis gives:—

C = 85·59	. .	C_{16} = 85·71
H = 14·40	. .	H_{16} = 14·29

The vapour-density was found to be 3·80 = 4 vol.; calculation gives 3·86.

THE

QUARTERLY JOURNAL

OF THE

CHEMICAL SOCIETY.

XXVI.—*On the Produce obtained from Barley sown in Rocks of various ages.*

By Charles Daubeny, M.D., F.R.S., F.C.S.

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It has been much disputed amongst geologists, whether there be any evidences derivable from the structure of the rock-formations which constitute the crust of the globe, such as should lead us to infer that any of those lying near to the bottom of the series had been deposited at a period antecedent to the commencement of animal and vegetable life.

The affirmative of this proposition is naturally taken by those who contend for the old, and, until lately, universally received opinion, that the great classes into which animals and vegetables are divided appeared upon the earth, not simultaneously, but successively; the invertebral class in the former, and the cryptogamia in the latter, having been first created, in accordance, as theory suggests, with the more chaotic condition of the earlier stages of our planet; whilst the vertebrata and the phanerogamia were brought into being afterwards, when circumstances became more favourable to the existence of plants and animals accomplishing a greater variety of functions, and requiring, therefore, a more elaborate and delicate organisation.

Such an opinion must be distinguished from the views of the author of the "Vestiges," as it may be entertained without any participation in the doctrine of transmutation of species; in the one case, it being conceived that organisms as perfect and as complicated as the conditions of the earth admitted, were created in every stage of the world's

progress, and, therefore, that higher types of the classes which were in existence, often preceded lower ones; in the other, the superior types, even under possible external conditions, requiring to be elaborated out of the inferior, and, therefore, necessarily succeeding them.

The negative, however, of both these hypotheses is equally implied in the attempts made by Sir Charles Lyell and his followers to convince us, that the animals which stand highest in the order of being, might all, with the exception of man, have existed at the earliest periods of the earth's creation, no less than those humbler forms of organisation of which such abundant vestiges have been preserved; since, if such a position be tenable, there would then be no apparent reason why the oldest stratified rocks should not have teemed with the remains of animal life as generally, and as copiously, as is found to be the case with respect to those deposited at the present day.

It is not my purpose to detain you with the arguments by which these two theories are respectively maintained; the former supported by the general tenor of the observations hitherto made with respect to the organic remains contained in rocks of different ages; the latter fortified by an appeal to certain exceptional cases, in which the remains or foot-tracks of animals of higher organisation have been found associated with the more characteristic fossils of the stratum; and, consequently, must be inferred to date their existence from a period of greater antiquity than our preconceived notions would have led us to assign to them.

But with regard to the other question, which relates to our recognition of rocks formed antecedently to the existence of organic life, or at least deposited when living beings were just beginning to appear, it cannot, I think, be disputed, but that there is a *primâ facie* case, at least, in favour of it, in the entire absence of organic remains from many rocks lying below the great Silurian formation, which have been well explored; and also from the gradual dying out, as it were, of the same as we descend in the series.

"Thus," as Sir R. Murchison observes, "in Bohemia, as in Great Britain, and in portions of North America, the lowest zone containing fossil remains is underlaid by very thick buttresses of earlier sedimentary accumulations, whether sandstone, schist, or slate, which, though occasionally not more crystalline than the fossiliferous beds above them, have yet afforded no sign of former beings."

The reply to this argument is made by an appeal to our ignorance; by reference to the many cases of metamorphic action that occurred at later periods of the earth's history, from which an entire obliteration of the organic remains of a rock appears to have resulted; and by

suggesting that the chances of metamorphic action having taken place are multiplied in proportion to the antiquity of the formation with which we have to deal.

In considering this question, it occurred to me to ask, whether there were not certain products of the operations of life which might escape destruction, even if all external indications of them were obliterated; and, if so, whether they ought not to remain as permanent monuments of beings that once existed, even after this supposed metamorphic action had remodelled the beds in which they were deposited.

It is now many years since* I satisfied myself of the existence of phosphoric acid in so many secondary limestones, that I was led at the time to infer that this ingredient existed almost universally; and at present its occurrence even amongst metamorphic rocks is generally admitted, not only from the indirect evidence arising from the fact that plants are able to draw this necessary principle in sufficient quantities from the soil resulting from the decomposition of such rocks, but also by direct analysis, which has established its presence in them.

If this be the case, I see no reason why the earliest rocks with which animal life was associated should not still retain the phosphoric acid, which must have formed an integral part of their organisation, and, therefore, might not afford, to a certain extent at least, a presumption in favour of the presence of organic remains before metamorphic action had changed altogether the original structure of the rock.

The occurrence, indeed, of phosphoric acid in a rock is no certain criterion of the former existence of animals, because we must assume it to have been present, in common with all the other necessary constituents of organic bodies, before any of the latter came into being; and because, also, we have examples of its appearance, as in the phosphorite rock of Estremadura, in a condition which compels us to ascribe its deposition to chemical forces alone.

When, for instance, Sir Charles Lyell, in his anniversary address for 1851, p. 36, alleges, that the discovery made by the Government surveyors of concretions containing between 30 and 40 per cent. of phosphate of lime in the Bala limestone bears witness to the existence of vertebrata in the most ancient seas, we are inclined to withhold our assent to such a proposition, until assured that this local accumulation of the substance in question could not have been brought together

* Report on Mineral and Thermal Waters: Brit. Assoc. Reports for 1836, p. 20.—Three Lectures on Agriculture, 1841, p. 46.

by those chemical operations which have worked so many changes in rocks, antecedently to, or at least independent of, the agency of living beings. But the converse of the proposition would seem less open to objection, for it is contrary to all analogy to imagine any class of animals to have existed, without leaving behind them some traces of the phosphoric acid, which seems, so far as we know, an universal concomitant of life in all its phases.*

These traces no doubt become fainter as we descend in the scale of organisation, and consequently may, in many instances, escape detection.

The main difficulty, indeed, in the investigation, arises from the minute quantity in which phosphoric acid exists, as compared with the other ingredients of a rock, as well as from the imperfection of our means of separating it, when intermixed, or combined with the other matters present.

I have tried to extract phosphoric acid from the slate of Skiddaw, of Bangor, and some others, operating upon several ounces of each by long-continued digestion in nitric acid, as recommended to me by Baron Liebig, but could not satisfy myself of the presence of this substance, although I suspected traces of it to exist in the instance of that from Skiddaw. I have, however, no confidence in my power of eliminating, by any chemical reagents at my disposal, from a mass of clay, stone, or loam, a portion of phosphoric acid which does not exceed $\frac{1}{10000}$th part of the entire mass; and yet such a proportion distributed over an acre of ground, which, to a depth of only one foot, contains at least 1600 tons of earth, would indicate more than 350 lbs. of phosphoric acid,—equivalent to that contained in a very large development of animals of the lower class.

But we may be sure that if any of those crops which contain in themselves nutriment for the higher grades of animals will grow in a particular rock, phosphoric acid in some shape or other must be present in it.

If any doubt exist on that head, I may refer in confirmation of it to the recent experiments of the Prince of Salm-Horstmar,†

* Lehmann (Physiological Chemistry) states that phosphate of lime occurs in every kind of animal tissue, in all animal fluids, in all protein compounds more especially. It probably plays an important part in the metamorphosis of the animal tissues, and especially in the formation and in the subsequent changes of animal cells.

Schmidt found, in the inner side of the mouth of Unio and Anodonta, no less than 15 per cent. of phosphate of lime, 3 of carbonate of lime, and 82 of organic matter; so that the phosphate seems to be separated from the blood by this organ, for the purpose of cell-formation. It seems probable that the carbonate is converted in the animal into phosphate by the phosphorus it contains. The latter, however, would seem to arise from the reduction of phosphoric acid. I suspect that phosphoric acid will be found present in all nitrogenised structures, whether of animals or vegetables.

† Ann. Ch. Phys. [3], xxxii. 461, xxxv. 54.

which show, that if the soil be deficient in any of the seven essential elements of plants, of which phosphoric acid is one, no complete development of its parts will take place.

It would seem, therefore, at first sight, as if we had nothing else to do except to observe whether or not a soil was utterly barren, in order to assure ourselves of the presence of this ingredient; and such undoubtedly would be the case, provided we could ascertain that neither art nor nature had introduced any foreign body into the materials derived from the subjacent subsoil.

But I know not how this can be confidently predicated, even with reference to a newly-peopled country, much less in the case of one long cultivated, like our own; since it would be necessary to prove, not only that the surface had never been modified by the addition of any kind of manure, but also that no torrent or flood had at any time spread over it materials derived from the country adjacent.

It seemed to me therefore, that it would be more satisfactory to try the experiment on a small scale, by bringing away from the spots, the subsoil of which it was my wish to test, a sufficient quantity of the pure rock to fill an open box, the dimensions of which should be about 2 feet square, and of nearly equal depth.

Into this, the material, after having been coarsely pulverised, was introduced; more or less pure sand being added to it, according as this was found necessary, in order to bring the whole into that state of consistency which appeared likely to render it, mechanically speaking, suitable for vegetation.

A given weight of barley, the amount of ash, and also of phosphoric acid, present in which had been ascertained by a previous examination, was then sown in each of the boxes. In the experiments made in 1852 and 1853, the quantity of barley sown weighed in each case 120 grains, from which were obtained 3·5 grains of ash, and as nearly as possible 1 grain of phosphoric acid; but finding this quantity unnecessarily large for the earth employed, only fifteen grains were introduced in 1854, which, from the results obtained, seemed to be amply sufficient.

Wishing to test in this manner the relative capacity of rocks of different ages to yield phosphoric acid to the crop which grew in them, I selected the following samples, which include most of the rock-formations, from the chalk to the lower Silurian or Cambrian series :—

1. The chalk from the neighbourhood of Brighton, Sussex.
2. The sand from the calcareous grit of Headington, near Oxford.

3. The oolitic limestone taken from the borders of the Cotswold Hills, near Cirencester, Gloucestershire.
4. The new red sandstone from Haffield, near Ledbury, in Herefordshire.
5. Pure dolomite from the magnesian limestone formation of Roche Abbey, in Derbyshire.
6. Slate taken from a spot near Dolgelly, designated by Professor Sedgwick as a rock lying below the Silurian strata, and apparently destitute of organic remains.
7. Clay slate from the foot of Skiddaw, in Cumberland, also regarded by geologists as lying very low in the series.

To these were added, in the present year, two samples of slate from N. Wales, both, so far as our examination has yet gone, totally destitute of organic remains, and both lying at the base of the whole series of rock-formations which have been described by Sir Roderick Murchison and Professor Sedgwick in that country.

These were—

8. The slate from the quarries of Nant Frangon, near Bangor; and
9. That from the quarries of Llanberris, in the same neighbourhood.

I also employed a sample of micaceous schist from Loch Lomond, procured through the kindness of Mr. Andrew Liddell, of Glasgow,—a rock in which metamorphic action had entirely obliterated all traces of organic life, if any such were ever present in it.

In order to afford a standard of comparison, there was added to these, in each of the three years, a box containing some of the soil of the Botanic Garden, Oxford, where the experiments were carried on, of which an analysis has been already given in my Bakerian Lecture, Phil. Trans. 1845, but which may be described briefly as a made soil of an argillaceous character, resting on the Oxford clay.

The results obtained are given in a connected view in the two tables which accompany this memoir (pp. 301, 302, and 303); and I have also constructed a diagram (p. 300), in which the relative quantities of phosphoric acid extracted from each of the rocks during the several years in which the barley was sown in them, are registered.

During the years 1852 and 1853, none of the rocks or soils experimented upon were manured, except that from the Botanic Garden; and yet it will be perceived that the crops grown in the former of these years were all sufficient to attest the fact, that a portion of phosphoric acid must have been withdrawn from the rock in which

they were reared. The proportion, however, varied very considerably; and if we regard the quantity yielded by the crop which was obtained from the Botanic Garden soil, as the normal amount which, under such circumstances, the crop was likely to extract from ground of about the average amount of fertility, we shall find that whilst 3·9 grains of phosphoric acid had been absorbed in this instance, no less than 7·73 was extracted from the rich marly sandstone of Ledbury; 2·38 from the chalk; 1·52 from the Headington grit; and quantities varying from 1½ to 1 grain from the remaining rocks.

So far, therefore, there appeared no striking inferiority on the part of the Cambrian or lower Silurian slates, to the oolite, the Headington grit, or the dolomite of Derbyshire; for the differences in the amount of phosphoric acid taken up by the crop in these several instances, were very inconsiderable. But the produce of the year succeeding seemed to indicate that, in the former cases, the deficiency arose from an actual want of phosphoric acid, whilst in the latter it was occasioned only by the necessity for a longer period of exposure, in order that the natural agents of decomposition should be enabled to develope, and render soluble, ingredients which were actually present in the rock, but which, at first, had not been available.

This, I think, may be inferred from the fact, that whereas the oolitic rock in 1853 supplied 4·1 gr. of phosphoric acid, the dolomite 6·53, and the Headington grit 5·55: the slate from Dolgelly, on the other hand, yielded only 0·05, and that from Skiddaw none at all.

In 1854, a similar deficiency in the amount of phosphoric acid obtained, was evinced by the two specimens of Welsh slates which I then operated upon; that from Bangor imparting little more than 0·8 of a grain of phosphoric acid to the barley sown in it, and from Llanberris none at all; there being, in fact, less phosphoric acid in the crop than in the grain sown.

The specimen of micaceous slate, likewise, which I obtained from the neighbourhood of Glasgow, only appeared capable of supplying about 0·6 of a grain of phosphoric acid to the crop which grew in it.

A similar argument, as it appears to me, might be deduced from the fact, that no large amount of lime in any shape at all, as compared with the other ingredients, was discoverable in the slates in question. Thus, after long digestion in nitric acid, the slate from Dolgelly yielded only 3·2 gr. in the 1000, or about 0·3 per cent.; the mica schist 1·6 in the 1000 gr.; the Bangor slate 1·23; the Skiddaw, only a mere trace; the Llanberris slate, none at all. After fusion with carbonate of soda, indeed, these slates, similarly treated, afforded

rather a larger quantity of lime, the rock from Dolgelly then indicating as much as 13·2 gr. to the 1000; the mica schist 4·85 gr.; that from Bangor 4·1 gr.; and from Llanberris 2·2. The Skiddaw slate alone, under neither of these methods of procedure, gave indications of more than a trace of lime. These quantities, however, are all very small in relation to those ordinarily existing in rocks which contain organic remains, unless, indeed, in cases where we may on other grounds suspect a removal of the lime originally present, or a substitution for it of some other ingredient, to have taken place.

Now, as in the case of phosphoric acid, although the presence of lime proves in itself nothing as to the existence of animal or vegetable life cotemporaneously to the deposition of the rock, its absence would seem to indicate the want, and its deficiency the paucity at least, of lime-secreting beings.

It remains to be seen whether rocks of equal antiquity contain lime in such a condition—that is, so disseminated through the rock—as to lead to the contrary inference; for its occurrence in veins, or in alternating strata, would prove nothing, inasmuch as chemical forces alone might have been capable of bringing it there, and of producing the arrangement which it exhibits.

To return, however, to the case of the phosphoric acid, it might be said that the failure in these instances arose, not from the want of this ingredient, but from some mechanical or other unsuitableness in the rock for rearing a crop of the above description; but this objection was obviated by adding, in 1854, to the same sample of Dolgelly and of Skiddaw slates which had been made the subject of experiment in the two preceding years, a portion of phosphate of lime and of nitrate of soda.

The same trial was also made upon the two Welsh slates obtained in 1854, and in these instances in a manner even more conclusive, because the manured and unmanured rock was experimented upon at the very same time.

The great increase of crop obtained in all the four instances by manuring, sufficiently evinces that there was no mechanical impediment offered by any of those samples of rock to the growth of barley; the following being the results obtained:—

In Dolgelly slate, the phosphoric acid extracted from the rock in 1853 was only 0·05; in 1854, the rock being manured, 1·06.

Skiddaw slate	.	in 1853, unmanured	0·00
„ „	.	„ 1854, manured .	1·93

Slate from Bangor	in 1854,	unmanured	0·08
„ „	„ „	manured .	1·71
„ from Llanberris	„ 1854,	unmanured	0 00
„ „	„ „	manured .	1·00 gr.

The same inference may probably be drawn from the fact, that in those rocks which evinced a deficiency in phosphoric acid, the proportion of straw to grain exceeded the average, so that it may be concluded that the barley made an effort to develope itself, and proceeded in its growth, until it was arrested by the want of phosphoric acid.*

As this ingredient is not uniformly distributed through all the parts of a growing plant, but is found principally in the grain, and even in this is confined to the gluten, starch being almost destitute of it, † it seemed to me desirable not to content myself, in every instance, with merely calculating the probable amount of phosphoric acid from that of the ash obtained, but in some cases to determine it by actual experiment; and accordingly it will be found, by reference to the table, that in the case of the Bangor, Skiddaw, Llanberris, and Dolgelly slates, less phosphoric acid was detected in the ashes than is normally present in the same amount of barley.

It must be admitted that the above experiments, even though conducted upon a sound principle, do not go the length of substantiating the entire absence of phosphoric acid in any of the cases examined, except in that of the Llanberris slate, where, as will be seen, there was even at first less phosphoric acid in the crop than in the grain previously sown, whilst in the others we always observed in the first year a small increase, amounting in the case of the Bangor slate to about $\frac{8}{10}$ of a grain; in that of the Dolgelly rock, to about $1\frac{1}{2}$ gr.; in that of the Skiddaw slate, to 1·2; and in the micaceous rock from Loch Lomond, to about $\frac{6}{10}$ of a grain.

Nevertheless, the marked diminution which, in these cases, took place in the second year, serves to show that the first crop had really taken up nearly all which the rock was able to afford; and in these cases the inference would seem to be, that we had approached the borders, at least, of the lower limit of organic existence; for, as the

* See the experiments recorded in the "Annales de Chimie" for 1851, by the Prince of Salm-Horstmar, on the growth of oats in boxes filled with pure sand or quartz, from which one or more of the substances usually present in soils and in the ashes of plants were excluded. When phosphoric acid was cut off, though the vegetative part of the plant, as the straw, continued, the seed was not produced, and the process of reproduction was arrested in the act of flowering.

† See my Bakerian Lecture, p. 239–40.

whole quantity of rock contained in each of the boxes exceeded 60 lbs. or 460,800 grains, we should have no right to calculate upon more than from about $\frac{1}{300000}$ part of phosphoric acid in the rock which yielded the largest amount of this ingredient, and little more than $\frac{1}{1000000}$ in that which supplied the smallest.

Now in the case of the Cambrian slate from Dolgelly, the stock of phosphoric acid appeared the second year to be *nearly*, and in that from Skiddaw, *wholly* exhausted, although, by the addition of phosphate of lime to each, they were brought back, as will be seen, to more than their original fertility.

If, then, we compare the above proportions of phosphoric acid with those ascertained by the most recent investigations to exist in secondary limestones, or in soils derived from them, we shall find an enormous disproportion between the two; few of the latter that have been analysed appearing to contain less than one part of phosphoric acid in 10,000, and many probably as much as 1 part in the 1000.

If it be objected that the phosphoric acid might be locked up in the rock in such a manner as to prevent its being given out to the growing crop, it may be replied that we have no right to infer the existence of a body which has neither been detected by direct chemical analysis, nor shown to be present by the indirect method resorted to, until at least more refined researches shall either have determined its presence, or have pointed out the manner in which, after having been once deposited in the rock, it may have been dissipated by the metamorphic action which subsequently took place.

It may also be objected, that my experiments are too limited in number and extent to warrant any general conclusions being deduced from them; nor, indeed, have I the presumption to suppose, that they alone are capable of settling so large a question as that which has been mooted in this paper.

I may, however, remark, that whilst in all the secondary rocks I examined, the usual proportion of phosphoric acid was discoverable by my method, a marked deficiency in this ingredient was perceived in every one of the samples taken from the bottom of the Silurian or of the Cambrian series which I had collected.

It may, moreover, be pointed out, that these samples were chosen, not from one locality, but from a number of places, for the most part quite remote one from the other, in England, Scotland, and Wales,—and that, in the case of the Bangor slate, the rock employed consisted of the powder rubbed off from a great variety of slates, taken from all parts of that extensive quarry, by the grinding or sawing process to

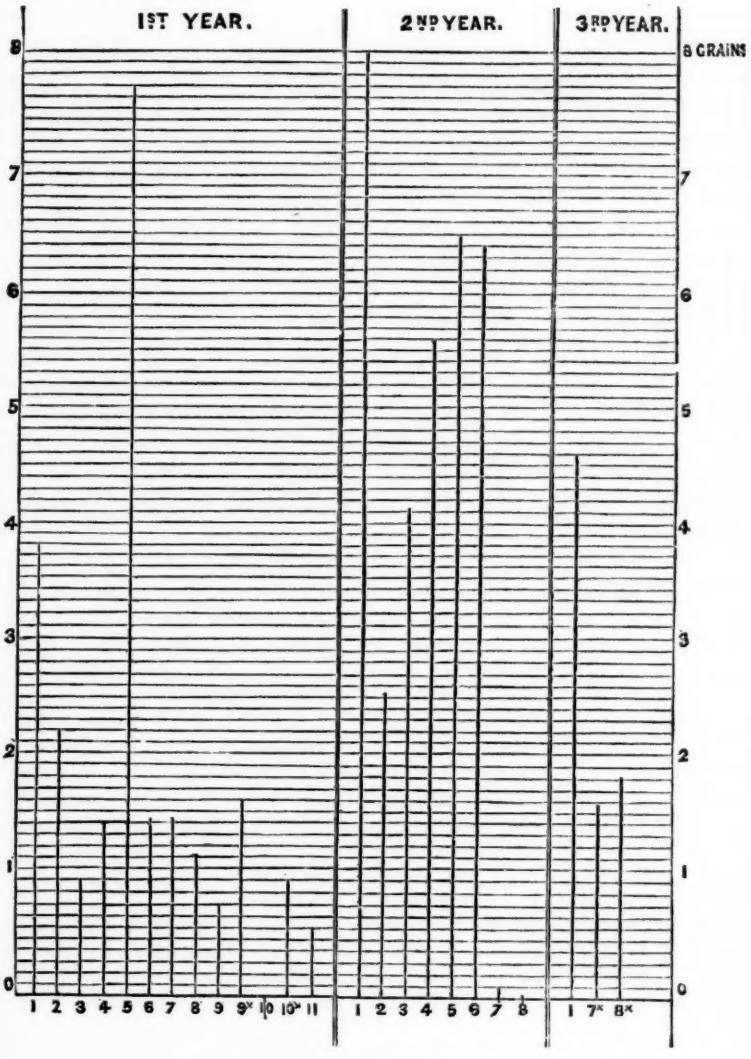
which they are subjected in order to bring them to an uniform size; and that they may therefore be presumed to present a fair average of the rock in general.

Indeed, when we recollect that not a trace of any organic body has been detected by the most careful examination, notwithstanding the vast quantities of this slate that have been exposed to observation within the last century, in consequence of the enormous demand that has arisen for the material, both at home and abroad, it is evident that, if organic remains were ever present, the most complete metamorphic action must have operated throughout the mass, in order to bring about so total an obliteration of them; nor could such a process have taken place without diffusing the phosphates throughout the rock, so as to afford traces of it everywhere.

At any rate I hope to have succeeded in opening a line of inquiry, which, if further pursued, may lead to the future elucidation of this problem, and, at the same time, may have an immediate practical bearing upon agriculture itself, by pointing out which of the rock-formations are most likely to be deficient in phosphoric acid, and, therefore, most susceptible of amelioration by manures containing that principle.

TABLE,

Showing the relation between the amount of phosphoric acid present in the barley sown, and in the crop obtained from it, in the several soils below-mentioned :—



REFERENCES TO THE NUMBERS.

1. Botanic Garden Soil.
2. Chalk of Brighton.
3. Oolite, Cirencester.
4. Sand, Headington.
5. Sandstone, Ledbury.
6. Dolomite, Roche Abbey.
7. Clay Slate, Dolgelly.
7*. Ditto, manured.
8. Clay Slate, Skiddaw.
8*. Ditto, manured.
9. Clay Slate, Bangor.
9*. Ditto, manured.
10. Clay Slate, Llanberris.
10*. Ditto, manured.
11. Mica Schist, Glasgow.

Rock in which the Barley was sown.	Produce from the Barley sown in 1852 and 1853.		Ash obtained from the Crop in				Amount of Phosphoric Acid present in the Crop of				Relation between the Organic and Inorganic Matter existing in the Crop obtained in				Relation between the two Crops, the Ratio being in	
	Unmanured.															
	1852.	1853.	1852.		1853.		1852.		1853.		1852.		1853.		1852.	1853.
1. Chalk, Brighton:—	—	—	—		—		—		—		—		—		—	—
Grain	327·0	267·0	.....	7·0	.....	8·0	By calculation ..	2·00	By experiment	2·50	Grain as..	100	100		Grain as	100 81·0
Straw	1233·0	630·0	.....	77·0	.....	54·5	By experiment ..	1·38	By calculation	0·97	Ash	2·11	3·00		Ash as	100 114·0
Total.....	1560·0	897·0		84·0		62·5		3·38		3·47	Straw as..	100	100		Straw as	100 51·5
Weight of Barley sown	120·0	120·0	Weight of Ash in Barley sown	3·5	.....	3·5	Phosphoric Acid in Barley sown	1·00	.....	1·00	Ash	6·35	8·6		Ash as	100 70·5
Gain.....	1440·0	777·0	Gain	80·5	Gain..	59·0	Gain	2·38	Gain ..	2·47						
2. Sand, from Headington, Oxfordshire:—																
Grain	175·0	396·0	.....	5·0	.....	12·0	By calculation ..	1·42	By experiment	4·20	Grain as..	100	100		Grain as	100 225·0
Straw	665·0	1680·0	.....	62·0	.....	130·0	By calculation ..	1·19	By calculation	2·35	Ash	2·85	3·02		Ash as	100 240·0
Total.....	840·0	2076·0		67·0		142·0		2·52		6·55	Straw as..	100	100		Straw as	100 254·0
Weight of Barley sown	120·0	120·0	Weight of Ash in Barley sown	3·5	.....	3·5	Phosphoric Acid in Barley sown	1·00	.....	1·00	Ash	9·40	7·55		Ash as	100 210·0
Gain.....	720·0	1956·0	Gain	63·5	Gain..	139·5	Gain	1·52	Gain ..	5·55						
2. Oolitic Limestone, Cotswold Hills, near Cirencester:—																
Grain	142·0	370·0	.....	3·5	.....	13·0	By calculation ..	1·00	By calculation	3·7	Grain as..	100	100		Grain as	100 264
Straw	698·0	920·0	.....	54·0	.....	79·0	By calculation ..	0·97	By calculation	1.4	Ash	2·4	3·5		Ash as	100 371
Total.....	840·0	1290·0		57·5		92·0		1·97		5·1	Straw as..	100	100		Straw as	100 132
Weight of Barley sown	120·0	120·0	Weight of Ash in Barley sown	3·5	.....	3·5	Phosphoric Acid in Barley sown	1·00	.....	1·0	Ash	7·7	8·6		Ash as	100 146
Gain.....	720·0	1170·0	Gain	54·0	Gain..	89·5	Gain	·97	Gain ..	4·1						
4. Red Sandstone, Ledbury, Herefordshire:—																
Grain	769·0	410·0	.....	20·5	.....	15·5	By calculation ..	5·85	By experiment	5·60	Grain as	100·0	100·00		Grain as	100 53·5
Straw	1991·0	1250·0	.....	159·0	.....	104·1	By calculation ..	2·88	By calculation	1·80	Ash	2·68	3·78		Ash as	100 75·0
Total.....	2760·0	1660·0		179·5		119·6		8·73		7·40	Straw as	100·0	100·00		Straw as	100 62·5
Weight of Barley sown	120·0	120·0	Weight of Ash in Barley sown	3·5	.. ..	3·5	Phosphoric Acid in Barley sown	1·00	.....	1 00	Ash	8·00	8·40		Ash as	100 65·0
Gain.....	2640·0	1540·0	Gain	176·0	Gain..	116·1	Gain	7·73	Gain ..	6·40						
5. Magnesian Limestone, Roche Abbey, Derbyshire;—																
Grain	227·0	496·0	.....	5·5	.....	17·3	By experiment ..	1·50	By calculation	4·95	Grain as	100·00	100·00		Grain as	100 213·0
Straw	793·0	1470·0	.....	54 0	.....	143·0	By calculation ..	0·97	By calculation	2·58	Ash	2·42	3·46		Ash as	100 314·0
Total.....	1020·0	1966·0		59·5		160·3		2·47		7·53	Straw as	100·0	100·00		Straw as	100 186·0
Weight of Barley sown	120·0	120·0	Weight of Ash in Barley sown	3·5	.....	3·5	Phosphoric Acid in Barley sown	1·00	.....	1 00	Ash	6·85	9 80		Ash as	100 265.0
Gain.....	900·0	1846·0	Gain	56·0	Gain..	156·8	Gain..	1·47	Gain ..	6·53						

Rock in which the Barley was sown.	Produce from the Barley sown in	Ash obtained from the Crop in
	1854.	1854.
6. Micareous Slate, near Glasgow :—	Unmanured.	
Grain	60 0	1·30
Straw	342·0	28·30
Total.....	402·0	29·60
Weight of Barley sown..	15·0	Weight of Ash in Barley sown .. ·44
Gain.....	387·0	Gain .. 29·16

	1854.		1854.	
	Unmanured.	Manured.	Unmanured.	Manured.
7. Bangor Slate :—				
Grain	75·0	330·0	..... 2·20	7·00
Straw	294 0	1222·0	..... 18·00	71·00
Total.....	369·0	1552·0	20·20	78·00
Weight of Barley sown..	15·0	15·0	Weight of Ash in Barley sown .... 0·44	·44
Gain.....	354·0	1537·0	19·76	67·66
8. Llanberris Slate :—				
Grain	4·0	164·0	..... 0·20	4·70
Straw	27·0	466·0	..... 2·30	27·80
Total.....	31·0	630·0	2·50	32·50
Weight of Barley sown..	15·0	15·0	Weight of Ash in Barley sown .... ·44	·44
Gain.....	16·0	615·0	2·06	32·06

	1852.	1853.	1854.	1852.		1853.	1854.
	Unmanured.	Unmanured.	Manured.	Unmanured.		Unmanured.	Manured.
9. Cambrian Slate, near Dolgelly :—							
Grain	184·0	138·0	330·0	.....	5·0	2·2	9·50
Straw	836·0	155·0	448·0	.....	54·5	17·7	26·00
Total.....	1020·0	293·0	778·0		59·5	19·9	35·50
Weight of Barley sown..	120·0	120·0	15·0	Weight of Ash in Barley sown	3·5	3·5	·44
Gain.....	900·0	173·0	763·0	Gain	56·0	16·4	35·06
10. Clay Slate, from Skiddaw, Cumberland :—	Unmanured.	Unmanured.	Manured.				
Grain	290 0	127·5	350·0	.....	7·6	2·8	10·10
Straw	910·0	150·0	537·0	.....	68·0	14·8	34·10
Total.....	1200·0	277·5	887 0		75·6	17·6	44·20
Weight of Barley sown..	120·0	120·0	15·0	Weight of Ash in Barley sown	3·5	3·5	·44
Gain.....	1080·0	157·5	872·0	Gain	72·1	14·1	43·76
Soil of the Botanic Garden, Oxford, being made ground resting on the Oxford Clay :—	Manured.	Manured.	Manured.	Manured.		Manured.	
Grain	428	591	565	.....	9·5	17·0	16·00
Straw	1132	1730	1695	.....	127·0	178·0	100·00
Total.....	1560	2321	2260		136·5	195·0	116·00
Weight of Barley sown..	120	120	15	Weight of Ash in Barley sown	3·5	3·5	·44
Gain.....	1446	2201	2245	Gain	133·0	191·5	115·56

Amount of Phosphoric Acid present in the Crop of		Relation between the Organic and Inorganic Matter existing in the Crop obtained in		Relation between the two Crops, the Ratio being in	
1854.		1854.			
By calculation	0·182	Grain as.	100·00		
By calculation	0·510	Ash	2·16		
	·692	Straw as.	100·00		
Phosphoric Acid in Barley sown	·125	Ash	6·80		
Gain	·567				

1854.				1854.		1854.	
Unmanured.		Manured.		Unmanured	Manured.	Unmanured	Manured.
By calculation	0·640	By experiment	0·560	Grain 100	Grain 100	Grain 100	440
By calculation	0·322	By calculation	1·280	Ash.. 2·9	Ash.. 2·1	Ash.. 100	317
	0·962		1·840	Straw 100	Straw 100	Straw 100	410
Phosphoric Acid in Barley sown	0·125		·125	Ash.. 6·1	Ash.. 5·8	Ash.. 100	394
Gain	0·837	Gain	1·715				
By calculation	0·062	By calculation	0·652	Grain 100	Grain 100	Grain 100	4100
By calculation	0·041	By calculation	0·500	Ash.. 5·0	Ash 2·86	Ash.. 100	2350
	0·103		1·152	Straw 100	Straw 100	Grain 100	1730
Loss	·22	Phosphoric Acid in Barley sown	·125	Ash.. 8·5	Ash.. 6·5	Ash.. 100	1200
Phosphoric Acid in Barley sown	0·125	Gain	1·027				

1852.		1853.		1854.		1852.	1853.	1854.	1852.	1853.	1854.
Unmanured.		Unmanured.		Manured.							
By experiment	1·500	By experiment	0·55	By experiment	1·260	Grain 100	100	100·	Grain 100	72·5	180·0
By calculation	0 970	By experiment	0·50	By calculation	0·470	Ash.. 2·70	1·60	2·87	Ash.. 100	75	180
Total..	2·470	Total ..	1·05	Total....	1·730	Straw 100	100	100·	Straw100	18·0	53·0
Phosp. acid present in Barley sown	1·00		1·00		·125	Ash.. 6·50	11·4	5·80	Ash.. 100	18·5	53·5
Gain ..	1·47	Gain ..	0·05	Gain....	1·605						
By experiment	1·0	By experiment	0·25	By experiment	1·400	Grain 100	100·0	100·	Grain 100	44	121
By calculation	1·2	By calculation	0·26	By calculation	0·660	Ash.. 2·62	2·2	2·88	Ash.. 100	37	133
Total ..	2·2	Total ..	0·51	Total....	2·060	Straw 100	100·0	100·	Straw100	16·5	59
Phosp. Acid present in Barley sown	1·0	Loss ..	0·49		·125	Ash.. 7·50	9·9	6·30	Ash.. 100	21·6	50
Gain ..	1·2	Phosp. Acid present in Barley sown	1·00	Gain....	1·935						
By experiment	2·6	By experiment	5·9	By experiment	2·840	Grain 100	100·0	100·	Grain 100	137	151
By calculation	2·3	By calculation	3·2	By calculation	1·800	Ash.. 2·88	2·88	2·83	Ash.. 100	179	169
Total ..	4·9	Total ..	9·1	Total....	4·640	Straw 100	100·0	100·	Straw100	153	150
Phosp. Acid present in Barley sown	1·0		1·0		·125	Ash 10·30	10·30	5·90	Ash.. 100	140	78·5
Gain ..	3·9	Gain ..	8·1	Gain....	4·515						

XXVII.—*Notice of Further Experiments as to the Reduction of Metallic Oxides by the Peroxide of Barium.*

By B. C. Brodie, F.R.S.,
SECRETARY TO THE CHEMICAL SOCIETY.

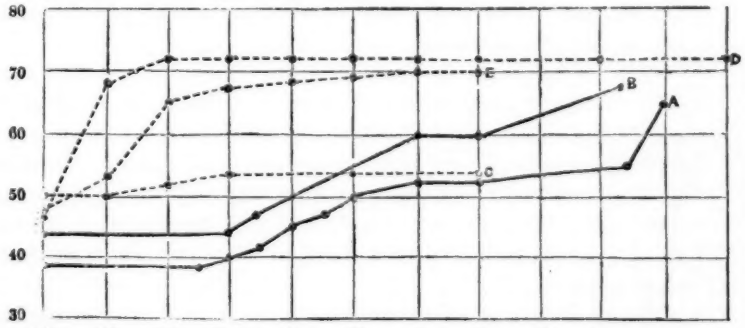
The following experiments were made in continuation of an inquiry relating to the laws of the formation of the elemental bodies, which appeared some time since in the "Transactions of the Royal Society." To render them intelligible, I may briefly recall the general results of that investigation.

It was known from the experiments of Thénard, that when the peroxide of hydrogen is placed in contact with certain metallic oxides, both substances are decomposed. This decomposition, which was not in harmony with prevalent ideas as to the nature of chemical decompositions, had received the occasional attention of chemists, but never been made the subject of experiment. It occurred to me that this event was a chemical change of a peculiar kind, in which two particles of oxygen fulfilled the same function and produced the same results as in ordinary decompositions were produced by the particles of two elements,—as, for example, of oxygen and hydrogen,—and that the reduction which took place was due to the chemical combination of the oxygen from the peroxide of barium with the oxygen from the reduced oxide. From this point of view, I made experiments as to the ratio in which the oxygen was evolved from the two substances. These experiments, while they confirmed these views, have opened out a new and further field of research. Experiment showed that the loss of oxygen from the reduced oxide bore a definite, but yet a variable, ratio to the loss from the peroxide of barium; that in all cases this ratio was comprised between two limits; the amount of reduction might be almost indefinitely diminished, in which case the action of the metallic oxide approached to that action of platinum or carbon which goes by the name of catalysis; and that, by changing the circumstances, the amount of reduction might be so increased as to approach very closely to a loss of equal equivalents of oxygen from the two substances. This loss of equal equivalents was realised in the case of the action of a mixture of iodine and water upon peroxide of barium, in which experiment water itself may be regarded as the oxide reduced. The ratios intermediate between these limits indicated a remarkable law. This ratio varied with several circumstances,—with the nature of the chemical substance reduced, with the temperature, and with the mass. It appeared that when the relative proportion of the

substances was varied, other circumstances being the same, this ratio changed, not continuously, but by intermittent steps; so that while at certain points there appeared to be a continuous increase of loss, as the quantity of the metallic oxide was increased, at certain other points, this quantity might be very greatly varied without any alteration of the ratio. Since these experiments, the existence of this law in other cases of the action of mass has been placed beyond a doubt by the researches of Bunsen and of Debus.

The method by which my experiments were conducted was not sufficiently exact to bring out these numerical results with the accuracy desirable, and I turned my attention to other modes of effecting this object. The plan I have adopted is that of acting upon weighed quantities of the peroxide of barium with solutions of metallic salts of known strength.

I have thrown into the annexed table the result of some of these experiments, which were made with solutions of nitrate of silver. The oxygen was measured by the amount of silver reduced, which was determined as chloride. The ordinates measure this loss of oxygen, the oxygen in the peroxide being estimated at 100. In the series marked A and B, the temperature was varied, while the strength of the silver solution was the same, the quantity of which taken corresponded to two equivalents in relation to the oxygen in the peroxide. The variations of temperature are indicated by the abscissa. Different preparations of the peroxide of barium were used in the two series of experiments. In series A, assuming the oxygen in the peroxide as 100, the oxygen corresponding to the silver reduced at the temperatures 100°, 75°, 70°, 65°, 60°, 55°, 50°, 40°, 30°, 7°, 0°, was 39, 39, 40, 42, 45, 47, 50, 52, 52, 55, 65. In series B, the oxygen corresponding to the silver reduced at the temperature 100°, 70°, 65°, 40°, 30°, 8°, was 43, 44, 48, 60, 60, 67.



It will be perceived that in each of these series of experiments there are two intervals of constant action. These intervals lie, in both cases, between 100° and 75°, and between 40° and 30°. The exact length and position of these intervals, the experiments are not sufficiently numerous to determine. This indicates the existence of a law, in the case of temperature, analogous to the law of mass.

The dotted lines give the result of three series of experiments, in which the temperature and the strength of the solution were constant, but the quantity of the solution employed was varied. The abscissa in this case gives the amount of the solution taken, as measured by the oxygen equivalent to the amount of silver contained in it. Thus where the numbers 50, 100, 150, appear in the lower line, the solution employed contained ½ an equivalent, 1 equivalent, and 1½ equivalents of oxygen, relative to the amount of oxygen in the peroxide of barium. The experiments indicated by the line c were made at 100° C. The loss of oxygen corresponding to the quantities 50, 100, 150, 200, 300, and 400, were 50, 50, 52, 53·5, 53·5, 53 5. Here again appear two constant intervals of action, namely where the variation was from ½ to 1 equivalent, and from 2 to 4 equivalents.

The line *d* relates to experiments made with the same preparation of peroxide as in *c*, and with the same solution, but at a temperature of 14° to 15° C. The loss of oxygen, as given by experiment, corresponding to the quantities of solution indicated by the numbers 50, 100, 150, 200, 250, 300, 350, 400, 500, and 600, was 46·6, 68·2, 73·4, 73·6, 72·8, 72·7, 72·3, 71 6, 72·0, 71·5. The mean of the last eight experiments gives 72·7, which is the number given in the table. The experiments were made at the temperature of the air. The experiments 1, 2, 3, 4, were made at one time, the experiments 5, 6, 7, 8, 9, 10, at another. The slight variation which these latter numbers present is probably due to an alteration of temperature. In this case the action is constant after the quantity has been increased beyond 1½ equivalents.

The experiments E were made at a temperature of about 8° C., with the same preparation of peroxide as in the last series, but with a solution containing half the quantity of nitrate of silver, compared with the solutions used in the two preceding series. The amount of oxygen lost corresponding to the quantities 50, 100, 150, 200, 250, 300, 350, 400, was 48, 53, 65, 67, 68, 69, 70, 70. In this case the maximum action was reached when 3½ equivalents of the solution were employed.

There is yet a third variable besides temperature and absolute mass, which, from the very nature of the experiment, it is not possible

to render constant. The action varies, not only with the absolute quantity of the silver solution employed, but also with the strength of that solution. Now the amount of silver in the solution, from the very decomposition which takes place, must change at every moment of the experiment. This variation has, doubtless, an important influence on the result; and although it cannot be entirely eliminated, yet it is obvious that, in the case of large quantities of the solution, the relative alteration of the solution is much less than with small quantities, and it is probable, that after that point where the action becomes constant, this effect is so small as not to be perceptible. The variations exhibited in the above experiments are with some substances much greater than with others, and in certain cases do not exist. For example, a solution of chloride of gold gave almost the very same amount of reduced gold, whether the experiment was made at 100°, or at the temperature of the air, and whether the solution were concentrated, or diluted with many times its bulk of water. The reduced gold corresponded to a loss of about 80 parts of oxygen from the solution to 100 from the peroxide.

In a recent number of Liebig's Annalen, Professor Wöhler, who does not seem to be aware, either of the theoretical views which have been put forward, or of the experiments which have already been made upon this subject, states that when a solution of peroxide of hydrogen in hydrochloric acid is acted upon by peroxide of manganese, that the oxygen evolved is exactly twice the oxygen due to the decomposition of the peroxide of hydrogen alone. The probable cause of the deviation which, in any case, appears from this result, is the simultaneous decomposition of the peroxide of hydrogen by two operations which, in the present state of our knowledge, we must regard as distinct,—namely, by the chemical action of the metallic oxide, and by that action which is termed catalytic, and which is produced either by the oxide itself or by the reduced metal which is formed. On the nature of this so-called catalytic action, or on the propriety of this term, I am passing no opinion, but am simply referring to a fact. In the experiment with iodine, above alluded to, this latter operation is entirely eliminated, and it is possible that, in the form of Professor Wöhler's experiment, the same result may be obtained. In the numerous experiments, however, which I have myself made upon this subject, I have not absolutely attained this result, except in the single instance referred to. By acting upon a mixture of peroxide of lead and peroxide of barium with dilute acetic acid, I have obtained a loss of 90 parts of oxygen from the peroxide of lead, and with peroxide of nickel,

in one experiment, a yet greater loss; but in every experiment with similar substances there was a certain deficiency. An interesting case of the reduction of peroxide of manganese is afforded by the mineral pyrolusite. In four experiments with this substance, made with dilute acetic acid, in which one equivalent of peroxide of barium was taken respectively to 4, 2, 1, and 1 equivalents of the pyrolusite, the loss of oxygen from the pyrolusite, to 100 parts of oxygen in the peroxide of barium, was 49·8, 48·9, 49·1, 50·9. The amount of reduction, on the other hand, exhibited by the mineral braunite, was very trifling: the action of this substance was nearly the same as that of platinum.

XXVIII.—*Analysis of a Surface-soil from the Desert of Atacama.*

By Frederick Field.

On the confines of the Desert of Atacama, a few miles to the east of the port of Caldeca, in the north of the republic of Chile, the soil for many leagues round has a perfectly white appearance, exactly as though it had been covered by a recent fall of snow. On investigation, it appears to consist of a white crystalline matter, which extends to the depth of six or eight inches below the surface; and on digging one or two feet deeper, large quantities of water are discovered, highly impregnated with saline matter. If the white substance be carefully scraped away, leaving an apparently clean surface of sand exposed to the air, crystals gradually form, and in a few weeks the spot is as white as before. The following is the composition of the substance taken from many parts of the locality above mentioned, affording a pretty correct illustration of the surface-soil of this part of the desert of Atacama:—

100 grms. gave:

Soda . . .	27·17
Sulphuric acid .	42·60
Chlorine . .	9·63
Lime . . .	6·72
Magnesia . .	4·75
Water . . .	12·30

with traces of oxide of iron, potash, and carbonic acid.

Deducting an equivalent of sodium for the formation of the chloride, the following numbers are obtained:—

Sulphate of soda . . .	41·77
Sulphate of lime . . .	16·32
Sulphate of magnesia . .	13·75
Chloride of sodium . .	15·60
Water	12·30
	99·74

with traces of oxide of iron, and carbonates of lime and soda.

This substance is perfectly soluble in cold water, if added in sufficient quantities, and digested with it for a long time; dilute hydrochloric acid dissolves it readily, with scarcely perceptible effervescence. It is slightly alkaline to test-paper,—due, probably, to a trace of carbonate of soda. When dissolved in water at 100° F., and allowed to cool, it deposits large crystals of sulphate of soda. I have sent home a specimen of the soil, and also some crystals of sulphate of soda produced from it by simple solution and crystallisation. One pound of the soil produces more than its own weight of crystallised sulphate of soda.

I am now engaged upon an investigation of the subsoil, taken three feet below the surface of the desert.

NOTE.—I may mention, that should it be agreeable to the Fellows of the Society, I intend to send home the results of some investigations of soils, minerals, and waters, found in the Desert of Atacama. The mineral waters, especially from the interior of the desert, in the republic of Bolivia, seem to me to possess much interest.

XXIX.—*On some of the Thermo-electric Properties of the Metals Zinc and Silver.*

By RICHARD ADIE.

A zinc and silver thermo-electric couple is known to reverse the direction of the current of electricity generated by heating it, when the temperature of the joint is raised above 248°, as described by the late Professor Daniell in his Introduction to Chemical Philosophy, p. 468. This peculiar property I have made the subject of the following experiments, which I hope may prove interesting, for they

show how completely thermo-electrical currents are governed by resistance to conduction in the joints of the couples.

Experiment I.—A piece of zinc wire was soldered to a piece of silver by pure bismuth for a solder, and the joint was made strong with a large surface of bismuth in contact with the metals. On heating this couple by dipping the joint in oil raised to different temperatures, the reversal of the current alluded to above was observed; for temperatures under 250°, zinc was positive, and for temperatures above that point, silver was the positive element.

Experiment II.—The same zinc and silver as in the last experiment, with bismuth surface in contact with the metals, made as small as practicable. The heat was applied by dipping the joint in oil raised to various temperatures from 100° to 360°, and in all the silver was the positive metal. The peculiar property of the reversal of the current, as the temperature passed a certain point, had disappeared with a change in the joint, which had only increased its resistance to conduction.

Experiment III.—The same zinc and silver couple employed with a joint formed without solder. The two surfaces of the metals were cleaned, and bound firmly together with thread, with only small portions of each element in contact. The result of this experiment was the same as No. 2; the silver stood positive for all temperatures.

Experiment IV.—The same zinc and silver were joined by a bismuth soldering, so as to form a continuous straight wire, with a bismuth joint in it, of which the surface in contact with the metals was nearly equal to the section of the wires. When heat was applied to the zinc wire, about two-tenths of an inch from the joint, silver was positive for all temperatures. And when heat was applied in a similar manner to the silver wire, the zinc became the positive metal for all temperatures. In this experiment, *the direction of the flow of heat across the joint governed that of the thermo-electric current generated*; it is a result which I have met with in many other thermo-electrical couples tested in like manner.

Experiment V.—A piece of zinc wire cut in two halves formed the couple for this experiment, with the joint formed by tying them firmly together; for temperatures under 300°, this arrangement showed very slight thermo-electrical effects; for higher temperatures more decided evidence of electrical action was obtained, but the direction of the currents generated was not regular.

Experiment VI.—The same pieces of zinc as for the last experiment, No. 5, with a bismuth joint, formed in the same manner as for experiment No. 4. This formed a delicate thermo-electrical couple.

When the right side of the joint was heated, the left wire was positive; and when the left side was heated, the right became positive: these effects could be readily shown by grasping the wires in the fingers. A similar experiment was made with a silver wire cut in two.

Experiment VII.—A piece of silver wire and a bar of bismuth formed the couple for this experiment. It may be premised that bismuth is a metal strongly positive to every other, and that the object in view was to endeavour to exhibit it as a negative element For the joint, the point of the silver wire was heated in sulphur until it was thickly coated with a sulphide of silver, and the sulphuretted portion was tied firmly down to the bismuth. On heat being applied to the silver, the couple did not become active* till the temperature was near 400°, when the bismuth showed itself the positive metal. On heat being applied to the bismuth bar, near the joint, the couple became active as before, at a high temperature, *and silver stood as a positive thermo-electric element to bismuth.* The experiment was tried with a thin coat of sulphide on the silver, when the couple became active at a lower temperature; but bismuth then stood positive to silver when heat was applied on its side, as well as when heat was given on the silver side.

Experiments like these, showing the direction of thermo-electrical currents to be under control, can be multiplied in great variety.

XXX.—*On the Preparation of Methylic Alcohol.*

By William Gould, Student of University College.

Kane's process for the preparation of methylic alcohol, by saturating crude wood-spirit with chloride of calcium, and distilling over the water-bath, generally yields but a small quantity of the pure product. I have tried it with various qualities of commercial wood-spirit, and in most cases have obtained not more than two or three ounces of pure methylic alcohol from a gallon of the crude spirit. A specimen of Parisian wood-spirit was found to produce the greatest quantity of the pure alcohol; but even in that case the pure product was in small proportion to the original substance,—the greater quantity of the liquid consisting of lignone, acetone, empyreumatic oils, &c. To obtain pure lignone, crude wood-spirit was treated with an equal quantity of a saturated aqueous solution of chloride of calcium, whereupon a separation of empyreumatic oils took place,

* A delicate galvanometer showed no indication of the passage of an electrical current.

which floated to the surface, in quantity equal to at least one-eighth of the bulk of the original substance. This was separated, the lower stratum treated with dry chloride of calcium, and submitted to the process of upward distillation, dry chloride of calcium being added as long as any continued to be dissolved, by which a further quantity of the oils was thrown up to the surface; the solution was then distilled, and lignone obtained, which, after desiccation, boiled at 61° to 66°.

The oils separated by solution of chloride of calcium were treated with a solution of caustic alkali, which gave rise to a strong action, and evolved great heat. The resulting liquid was found to contain methylic alcohol, lignone, acetic acid, and some resinous substance.

When crude wood-spirit is treated with an equal volume of a strong solution of caustic potash or soda, a tolerably strong action takes place, accompanied by a rise of temperature, and formation of a homogeneous solution; on distillation the residue is found to consist of acetate of soda, with a small quantity of resinous matter: it yields a very large quantity of acetic acid.

The distillate was desiccated by carbonate of potash, saturated with dry chloride of calcium, and distilled at 100° C. The resulting compound of methylic alcohol and chloride of calcium was decomposed by water in the usual manner, and the methylic alcohol thus obtained was dehydrated by distilling over quick-lime. The product was in very much larger quantities than that which is obtained without the use of caustic alkali.

The liquid distilled off from the methylated chloride of calcium was treated with a solution of caustic potash, which separated some oils mixed with acetone, and a small quantity of methylic alcohol. In the first treatment by caustic alkali, the oils and acetone had been held in solution by the greater quantity of methylic alcohol then present. The potash solution was distilled, and the distillate, after desiccation, separated by dry chloride of calcium into methylic alcohol and pure acetone, the latter being soluble in water, from which it was again separated by chloride of calcium or potash.

The oils and acetone were separated by mixing with water, which dissolved the acetone, the oils separating out and floating to the surface. The acetone was precipitated from its aqueous solution by potash, and thereby separated from a small quantity of methylic alcohol which had dissolved in it.

Methylic alcohol and acetic acid are the principal substances contained in crude wood-spirit, acetone and oils being also found in comparatively small quantities.

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY.

November 6, 1854.

PROFESSOR GRAHAM, Vice-President, in the Chair.

The following donations were announced:—

"The Literary Gazette:" for July, August, September, and October, from the Publishers.

"The Journal of the Society of Arts:" for July, August, September, and October, from the Society.

"The Journal of the Photographic Society:" for July, August, September, and October, from the Society.

"The Pharmaceutical Journal:" for July, August, September, and October, from the Editor.

"The Quarterly Journal of the Geological Society:" from the Society.

"Sitzungsberichte der kaiserlichen Akademie der Wissenschaften in Wien."

"Berichte über die Verhandlungen der naturforschenden Gesellschaft in Basel."

The following gentlemen were duly elected Fellows of the Society:—

Robert Mortimer Glover, M.D., F.R.S.E., Royal Free Hospital, Gray's Inn Lane.

James Taylor, Esq., 5, Burchfield Terrace, East India Road.

Newton Samuelson, Esq., 11, Temple Court, Liverpool.

Henry M. Noad, Ph.D., Bark Place, Bayswater.

Robert Hunt, Jun., Esq., Government School of Mines, Sydney.

Isaac Newton Loomis, M.D., of Macon, in the State of Georgia, U.S.

The following gentlemen were duly elected Associates of the Society :—

Mr. Henry Buff, St. Bartholomew's Hospital.
Mr. Richard Tuson, St. Bartholomew's Hospital.

A paper was read :—

"On the Analysis of a Surface-soil from the Desert of Atacama :" by Frederick Field.

At the request of the Chairman, Dr. Williamson brought under the notice of the meeting a communication, "On some new Derivatives of Chloroform," by Mr. George Kay, a Student in University College, which had been published in the "Journal of the Chemical Society" during the recess; and Dr. Gilbert stated the result of an investigation by Mr. Lawes and himself, of the quantities of ammonia and nitric acid in rain-water.

November 20, 1854.

Dr. Williamson, Vice-President, in the Chair.

Mr. James Taylor was introduced, and admitted a Fellow of the Society.

The following donations were announced :—

"The Literary Gazette :" from the Publishers.
"The Journal of the Franklin Institute:" from the Institute.
"Memoirs of the Literary and Philosophical Society of Manchester :" vol. ii., from the Society.
"Seventeenth Annual Report of the Council of the Art-Union of London :" from the Art-Union.
"Comparative Statement of the different plans of Decimal Accounts and Coinage; by T. W. Rathbone, Esq. :" from the Author.
"Sur l'Electricité des Nuages orageux, par M. Quetelet :" from the Author.
"Jahrbuch der kaiserlich-königlichen geologischen Reichsanstalt, Wien."

Mr. Griffin made a verbal communication on some points relating to chemical notation, and expressed his intention of bringing the subject more formally before the Society on a future occasion.

December 4, 1854.

COLONEL PHILIP YORKE, President, in the Chair.

The following donations were announced:—

"Specimen of Surface-soil from the Desert of Atacama:" from Mr. F. Field.

"Specimen of Malachite (Australian):" from Mr. G. Whipple.

"The Quarterly Journal of the Geological Society:" from the Society.

"Silliman's American Journal:" from the Editors.

"A Lecture on the Importance of the Study of Chemistry as a Branch of Education," delivered at the Royal Institution, by Dr. Daubeny: from the Author.

"The Journal of the Society of Arts:" from the Society.

"The Journal of the Photographic Society:" from the Society.

A paper was read:—

"On the preparation of pure Pyroxylic Spirit, by William Gould:" communicated by Dr. Williamson.

December 18, 1854.

COLONEL PHILIP YORKE, President, in the Chair.

The following donations were announced:—

"Proceedings of the Literary and Philosophical Society of Liverpool during the Forty-third Session, 1853—54:" from the Society.

"The Literary Gazette:" from the Publishers.

"The Journal of the Society of Arts:" from the Society.

The following gentlemen were duly elected Fellows of the Society:—

Fletcher Norton, Esq., 5, Stanhope Street.
Charles Loudon Bloxam, Esq., King's College.
Charles W. Heaton, Esq., Lime Street.
John S. Abel, Esq., Coquimbo, Chili.

The following papers were read:—

"On the Produce obtained from Barley sown in Rocks of various ages:" by Charles Daubeny, M.D., F.R.S., F.C.S.

"Notice of further Experiments as to the Reduction of Metallic Oxides by the Peroxide of Barium:" by B. C. Brodie, F.R.S.

TITLES OF CHEMICAL PAPERS

IN

BRITISH AND FOREIGN JOURNALS,

PUBLISHED IN THE YEAR 1854.

A.

Acetone.—Researches on Acetone: by *G. Städeler*. Ann. Ch. Phys. [3] xlii. 227; J. pr. Chem. lxii. 115.

—— On the theory of acetone: by *G. Chancel*. J. pr. Chem. lxii. 320.

—— On the action of hydrochloric acid on a mixture of acetone and alcohol: by *James Spencer*. Chem. Soc. Qu. J. vii. 247.

Acid, Acetic.—Preparation of pure acetic acid on the large scale, from the distillation-products of wood: by *R. v. Reichenbach*. Pharm. J. Trans. xiii. 433.

—— Volumetric determination of the strength of acetic acid. Pharm. J. Trans. xiii. 405.

—— On a method of analysis applicable to the quantitative estimation of nitric and acetic acids: by *J. H. Gladstone*. Chem. Gaz. 1854, 398.

—— Estimation of acetic acid: by *C. G. Williams*. Pharm. J. Trans. xiii. 594.

Acid, Aconitic.—On the occurrence of aconitic acid in *Delphinium Consolida*: by *W. Wicke*. Ann. Ch. Pharm. xc. 98; J. Pharm. [3] xxvi. 79; Chem. Gaz. 1854, 388; Pharm. J. Trans. xiv. 278.

Acid, Angelicic.—On angelicic and cinnamic acid: by *L. Chiozza*. Ann. Ch. Phys. [3] xxxix. 435; J. pr. Chem. lxi. 231.

Acid, Anisamic.—On anisamic acid: by *N. Zinin*. Bull. de St. Pétersb. Cl. Phys.-math. xii. 236; Chem. Gaz. 1854, 250.

Acid, Anthranilic.—On anthranilic, benzamic, and carbanilic acids: by *W. B. Gerland*. Chem. Gaz. 1854, 61.

Acid, Arachinic.—On arachinic acid: by *Dr. Gössmann*. Ann. Ch. Pharm. lxxxix. 1.

Acid, Benzamic.—On benzamic acid: by *W. B. Gerland*. Ann. Ch. Pharm. xci. 185.

Acid, Benzoglycolic.—New method of preparing benzoglycolic acid: by *A. Gössmann*. Ann. Ch. Pharm. xc. 181, Chem. Gaz. 1854, 310.

Acid, Benzoic.—On the alcohol corresponding to benzoic acid: by *S. Cannizzaro*. Ann. Ch. Pharm. lxxxviii. 129.

—— An attempt to obtain the acids homologous with benzoic acid from the corresponding hydrocarbons: by *James Spencer*. Chem. Soc. Qu. J. vii. 245.

Acid, Boracic.—On some little-known reactions of boracic acid and the borates: by *Ch. Tessier*. Compt. rend. xxxix. 192.; Chem. Gaz. 1854, 358; J. pr. Chem. lxiii. 7.

—— On the production of boracic acid and ammonia by volcanic action: by *R. Warington*. Chem. Gaz. 1854, 419; Pharm. J. Trans. xiv. 234.

—— On the compounds of boracic acid and water with alumina: by *H. Rose*. Pogg. Ann. xci. 452; Chem. Gaz. 1854, 210; J. pr. Chem. lxii. 32.

—— Influence of boracic acid upon solution. Pharm. J. Trans. xiv. 231.

Acid, Capric.—Occurrence of capric acid in potato fusel-oil: by *S W. Johnston*. J. pr. Chem. lxii. 262.

Acid, Carbazotic.—On the physiological properties of carbazotic acid: by *F. C. Calvert*. Pharm. J. Trans. xiv. 232.

Acid, Carbonic.—Action of carbonic acid on quinine and cinchonine; formation of crystallised carbonate of quinine: by *M. Langlois*. Ann. Ch. Phys. [3] xli. 89; J. Pharm. [3] xxvi. 132.

—— On the use of hydrogen gas and carbonic acid gas to displace sulphuretted hydrogen in the analysis of mineral waters: by *W. B. Rodgers* and *R. E. Rodgers*. Sill. Am. J. [2] xviii. 213; Chem. Gaz. 1854, 410.

—— On an apparatus for estimating carbonic acid: by *S. de Luca*. J. Pharm. [3] xxiv. 398; xxv. 32.

—— Modification of the apparatus for the estimation of carbonic acid. J. pr. Chem. lxi. 99.

Acid, Cinnamic.—On angelicic and cinnamic acids: by *L. Chiozza*. J. pr. Chem. lxi. 231.

—— On angelicic and cinnamic acids: by *L. Chiozza*. Ann. Ch. Phys. [3] xxxix. 435.

Acid, Citric.—Substitutes for citric and tartaric acids and their salts, in dyeing. Pharm. J. Trans. xiv. 68.

—— On the improved manufacture of citric and tartaric acids, alone, or conjointly with the manufacture of bitartrate of potash, tartrate of soda and potash, nitrate of potash, binoxalate of potash, carbonate of soda, carbonate of potash, and certain citrates and tartrates (*continued*). Pharm. J. Trans. xiii. 313, 370.

—— On the action of citric, tartaric, and oxalic acids on cotton and flax fibres under the influence of dry heat and pressure of steam: by *F. C. Calveri*. Chem. Gaz. 1854, 440.

Acid, Ferricyanic.—On some compounds of ferricyanic acid with ethyl: by *H. L. Buff*. Ann. Ch. Pharm. xci. 253.

Acid, Formic.—On the presence of formic acid in the human secretions: by *D. Campbell*. Chem. Gaz. 1854, 52.

Acid, Gallic.—On the molecular constitution of tannin and of gallic acid: by *E. Robiquet*. J. Pharm. [3] xxvi. 29; Pharm. J. Trans. xiv. 182.

—— On the action of gallic and tannic acids on iron and alumina mordaunts: by *F. C. Calvert*. Chem. Gaz. 1854, 440.

Acid, Hippuric.—Presence of hippuric acid in the scales of *ichthyosis*: by *J. Schlossberger*. Ann. Ch. Pharm. xc. 378; J. Pharm. [3] xxvi. 397; J. pr. Chem. lxiii. 58.

—— On the formation of nitride of benzoyl from hippuric acid: by *Dr. Limpricht* and *von Uslar*. Ann. Ch. Pharm. lxxxviii. 133; Chem. Soc. Qu. J. vii. 191; J. pr. Chem. lxi. 511; J. Pharm. [3] xxvi. 72.

Acid, Hydriodic.—Action of hydriodic acid upon glycerine: by *Berthelot* and *De Luca*. Compt. rend. xxxix. 748.

Acid, Hydrochloric.—On the decomposition of sulphate and phosphate of lime by hydrochloric acid: by *Cari-Mantrand*. Compt. rend. xxxviii. 864; Chem. Gaz. 1854, 265.

—— On hydrochloric acid as a test for lead in English sulphuric acid: by *P. Bolley*. Ann. Ch. Pharm. xci. 113.

Acid, Hydrocyanic.—Spontaneous generation of hydrocyanic acid in a medicinal compound: by *J. T. Plumber*. Pharm. J. Trans. xiii. 633.

—— On a new body produced from aldehyde ammonia and hydrocianic acid: by *A. Strecker*. Ann. Ch. Pharm. xci. 349.

—— Detection of hydrocianic acid in a human body three weeks after death: by *M. Brame*. Compt. rend. xxxix. 968.

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Sill. Am. J. [2] xvii. 78—88.

Part II.—1. Relations of anhydrous carbonates and sulphates. 2. Homœomorphism of beryl, pyrosmalite, dioptase, and eudialyte. 3. Homœomorphism of pyrrhotine (magnetic pyrites), greenockite, breithauptite, copper-nickel, nepheline, cancrinite. 4. Homœomorphism of willemite, phenacite, and the species of the corundum group. 5. Homœomorphism of apophyllite, nagyagite, uranite, anatase, matlockite. 6. Homœomorphism of romeine, idocrase, cerasine, chiolite, braunite. 7. Homœomorphism of sylvanite, mispickel. 8. Homœomorphism of andalusite, topaz, staurotide. 9 Discrasite, witherite, arragonite, &c. 10. Augite and wollastonite. 11. Pyro-

lusite and gothite not closely homœomorphous. 12. Homœomorphism of monazite, lazulite. 13. Datholite and euclase. 14. Isodimorphism of tourmaline and calcite. 15. Observations on the formulas and relations of some species: euclase, datholite, and sphene; beryl and eudialyte; pyrrhotine and greenockite.

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1. On the relation of leadhillite in crystallisation to the anhydrous sulphates and carbonates.
2. On the so-called silico-titanates and silico-tantalates.
3. Tourmaline.

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—— Mineralogical notices: by *A. Kenngott*.

First Series.—Wien Akad. Ber. ix. 557: Zinkenite, 557; gypsum, 561; antimonide of silver, 568; arsenical pyrites (danaïte). 583; senarmontite, 587; liebenerite and gieseckite, 595; natrolite (brevicite), 603; quartz, 605; cryptolite, 607; ruby silver (Rothgültigerz), 609; diaspore, 610; needle iron ore, 610.

Second Series.—x. 179: Needle iron ore enclosed in sunstone, 179; pyromorphite, 180; arsenide of silver, 180; gold crystals from Vorōspatāk, 181; diamond, 182; baralite, 288; baralite, 289; cancrinite, 290; chalilite, 290; beckite, 292; aggregation of common and white iron pyrites, 293; felsōbanite, 294; berthierin, 295; new hydrated silicate and phosphate from Baveno [?] in Italy, 298; triplite from Norwich (Mass.), 611; aegyrine, 614; mica, 615.

Third Series.—xi. 12: Arragonite and calc-spar, 12; fluor-spar, 16 and 22; telluride of silver, 20; crucilite, 20.

Fourth Series.—xi. 290: Calcspar and arragonite, 290; quartz, 294; iron-glance and needle iron-ore enclosed in dichroite, 299.

Fifth Series.—xi. 378: Gypsum, 378, 380, 381, 382; polyhalite, 383; brogniartin (glauberite), 386; quartz, 387; chrysotil, 388; sp. gr. of iron-pyrites, 392.

Sixth Series.—xi. 604.

Seventh Series.—xi. 750: Alstonite, 750; sulphato-carbonate of barytes, 752; quartz, 756; copper-bloom and red copper ore, 757.

Eighth Series.—xi. 977: Sylvanite, 977; chiolite, 980; orpiment, 982; alstonite, 990.

Ninth Series.—xii. 22: Covellin, 22; ferruginous cobalt-glance, 24; crystalline forms of ehlite, jeffersonite, and sassolin, 26; composition of tourmaline, 29; new form of axinite, 41.

Tenth Series.—xii. 161: Unguharite, an independent species; funkite, an alteration of augite; heteromerite, an alteration of vesuvian.

Eleventh Series.—xii. 281: Baltimorite from Texas, 281; sp. gr. of iron pyrites, 286; galaktite, 289; chlorophyllite, 292; Harringtonite, 293; crystalline forms of matlockite, 295; hudsonite, 297; chalilite, 299; ficinite, 300.

Twelfth Series.—xii. 485: Fluolite from Iceland, 485; biotite, 492; carpholite, 505; boltonite, 508; leuchtenbergite, 510; nordenskioldite and grammatite, 513.

Thirteenth Series.—xii. 701: Crystalline form of diopside, 701; plumbocalcite, 701; quantity of alumina in augite, 702; couzeranite, 714; phlogopite, 717; vesuvian in opal, 721.

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LONDON:
WILSON and OGILVY,
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ERRATA IN VOL. VI.

Page 288, line 1, *for* 2 vols. *read* 4 vols.

„ 288, „ 9, *for* $C_6H_7K\,SO_4 = \left\{\begin{matrix}C_6H\\K\end{matrix}\right\}O, SO_3$ *read*

$$C_6H_7K, 2SO_4 = \left\{\begin{matrix}C_6H_7\\K\end{matrix}\right\}O, 2SO_3.$$

„ 303, „ 3, *for* 754·2 *read* 745·2.

„ 303, 17 lines from bottom, *for* 61·32 *read* 60·97

„ „ „ „ „ *for* 21·535 *read* 21·412

„ „ „ „ „ *for* 0·027134 *read* 0·02697

„ „ „ „ „ *for* 4·88 *read* 4·852.

ERRATA IN VOL. VII.

Page 275, 14 lines from bottom, *for* ethyl *read* methyl.

„ „ 23 „ „ *for* O_3 *read* O_8.

„ „ 15 „ „ *for* $C_{14}H_6O_6$ *read* $C_{14}H_{16}O_6$.

„ „ 10 „ „ *for* H_4 *read* H_{34}.